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Sulfur Contamination in the Florida Everglades: Initial Examination of Mitigation Strategies

By William H. Orem

Aerial View of Stormwater Treatment Areas (STAs)
in the Northern Everglades

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Abbreviations

ACME – Aquatic Cycling of Mercury in the Everglades project
APS - adenosine-5'-phosphosulfate
ASR – aquifer storage and recovery
ATP – adenosine triphosphate
BCNP – Big Cypress National Preserve
CERP – Comprehensive Everglades Restoration Plan
DOC – dissolved organic carbon
EAA – Everglades Agricultural Area
ENP – Everglades National Park
EPA – Environmental Protection Agency
Hg - mercury
LOX – Arthur R. Marshall Loxahatchee National Wildlife Refuge
MeHg - methylmercury
MSR – microbial sulfate reduction
N – nitrogen
P - phosphorus
PASTA – periphyton assisted stormwater treatment area
PRB – permeable reactive barrier
S – sulfur
$(SO_4)^{2-}$-S/L-day – sulfate concentration measured as sulfur equivalents per liter per day (a rate)
SRB – sulfate reducing bacteria
STA – stormwater treatment area
USEPA – United States Environmental Protection Agency (formal for EPA)
USGS – U.S. Geological Survey
WCA – Water Conservation Area

SUMMARY

● Sulfate in excess of 1 mg/L contaminates about 60% of the freshwater Everglades (background sulfate levels in the Everglades are estimated to be ≤ 1 mg/L).

● Excess sulfate originates from EAA canal discharge. Isotopic data is consistent with sulfur used in agriculture (current applications and legacy in soil) as a primary source of the excess sulfate. Deep groundwater could also contribute, however, currently available data does not support groundwater as a major source of sulfate to the Everglades.

● Sulfate entering the Everglades stimulates microbial sulfate reduction (MSR), production of sulfide, and methylmercury production. A unique combination of conditions in the Everglades, including high mercury deposition, sulfate contamination, and favorable environmental conditions (extensive wetland area, wet/dry cycles, high dissolved organic carbon) result in high levels of methylmercury production and bioaccumulation.

● Buildup of toxic sulfide in Everglades' soils from sulfate stimulation of MSR makes soils more reducing , impacts macrophyte growth, and may impact other flora and fauna. Greenhouse experiments show that growth of sawgrass is adversely affected by sulfide toxicity at sulfide levels above 9 ppm. Levels as high as 13-15 ppm have been observed in heavily sulfur impacted parts of the northern Everglades where sawgrass has been replaced by natural invasion by cattail.

● Sulfate loading can stimulate phosphate and ammonium release from wetland soils via a process referred to as internal eutrophication (Lamers et al., 1998). Mesocosm studies in the Everglades have demonstrated that sulfate loading at levels equivalent to those observed at sulfur-contaminated sites in the northern Everglades enhanced remobilization of ammonium, sulfate, and dissolved organic matter from soils to porewater and surface water.

● Current restoration plans to deliver more water to the Everglades will likely increase overall sulfur loads to the ecosystem, impacting areas that currently do not have elevated levels of sulfur. Delivery of sulfate contaminated water to areas like Everglades National Park, ARM Loxahatchee National Wildlife Refuge, and Big Cypress National Preserve through the canal system and may serve to exacerbate the harmful effects of sulfate on the ecosystem (Gilmour et al., 2007 a, b). Sheet flow over expansive marsh areas that reduces sulfate loading is preferable.

●Dry/rewet cycles have been shown to temporarily increase surface water sulfate concentrations (due to oxidation of reduced sulfur in soil), stimulating MSR and methylmercury production. Although dry/rewet cycles are a natural phenomenon in the Everglades, current water management practices and present conditions of sulfur-contaminated soils and high atmospheric mercury deposition make these cycles more damaging by exacerbating methylmercury production and bioaccumulation. Minimizing dry/rewet cycles would help limit methylmercury production in the Everglades.

● Surface water stored in underground aquifers (aquifer storage and recovery) may acquire significant additional sulfate through interaction with connate seawater or dissolution of gypsum in the underground reservoirs, and costs versus benefits of using this approach in water management need to be considered.

● Monitoring data suggests that the ecosystem response to declines (or increases) in sulfate loading is rapid. A decline in sulfate concentrations in surface water in the central Everglades during the late 1990s (probably due to changes in water discharge management) resulted in a rapid decline in methylmercury production and bioaccumulation here within 3-7 years.

● Because of the serious impacts of sulfate on the Everglades, and the rapid response of the ecosystem to reductions in sulfate loading, a comprehensive Everglades restoration strategy could include reduction of sulfur loads as a goal. Mitigation of sulfate contamination in the ecosystem could be multifaceted, and might incorporate reductions in the many uses of sulfur in agriculture, reduction of groundwater sources (if important), investigation of methods for passive sequestration of sulfate as solid-phase reduced sulfide, reengineering of existing stormwater treatment areas (STAs) for better sulfate sequestration, and consideration of active mitigation of sulfate in runoff water (nanofiltration, ion exchange) at the individual farm level.

● Existing macrophyte-dominated STAs remove limited amounts of sulfate from surface water, possibly due to slow rates of diffusion of sulfate into soil where sequestration occurs, limited availability of iron for metal sulfide precipitation, and limitations on substrate production for microbial sulfate reduction. Periphyton-dominated STAs (PASTAs) may provide more extensive floc to fuel microbial sulfate reduction and sequestration of sulfur.

● Engineering permeable reactive barriers (zero-valent iron/organic substrate combined) into the inflow and outflows of STAs may enhance their effectiveness for sequestering sulfate.

● Active mitigation strategies such as nanofiltration and ion exchange can be highly effective in removing contaminants like sulfate from water, but are expensive and subject to biofouling. Testing the use of active mitigation technologies at the individual farm level would provide cost/benefit information on this technology.

● The reduction of sulfate concentrations in the Everglades from current levels (60 mg/L at some sites) to levels approaching background ($\leq$ 1 mg/L) would be a desirable goal, but is unlikely to be achieved as long as current agricultural practices persist in the source area and flow path of water that feeds the Everglades. It is clear that any reduction in sulfate loads entering the Everglades will benefit the ecosystem's overall health. A multifaceted approach employing reduction in anthropogenic source loads of sulfur, and passive and active mitigation will help achieve lower overall sulfate levels in the Everglades, and resulting benefits.

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1. Introduction

Sulfate contamination of the Everglades is a serious water quality issue facing restoration of this ecosystem. Sulfate concentrations in some marsh areas are more than 60 times background concentrations, and sulfate in excess of background levels covers an estimated 60% of the freshwater Everglades (Orem et al., 1997; Stober et al., 1996 and 2001; Orem et al., 2004). The excess sulfate enters the Everglades in the discharge of canal water from the Everglades Agricultural Area (EAA). Excess phosphorus also enters the ecosystem in EAA canal water discharge (Koch and Reddy, 1992; Craft and Richardson, 1993; DeBusk et al. 1994; Zielinski et al., 1999). Existing data suggest that sulfur in fertilizer and soil amendments used in the EAA (both new additions and legacy sulfur in the soil) is a major source of excess sulfate entering the ecosystem (Bates et al., 2001 and 2002). Other potential sources of sulfate (including groundwater), however, need further investigation. The report by Gilmour et al. (2007b) in the 2007 South Florida Environmental Report provides a complete examination of the current state of knowledge of the sulfur contamination issue in the Everglades.

Sulfate discharged from canals or leaking through levees into the ecosystem spreads out over a large area since, unlike phosphorus, it is not removed to any great extent by plant uptake. Sulfate slowly diffuses into the anoxic soils (peats) underlying the Everglades and stimulates microbial sulfate reduction (MSR), producing toxic hydrogen sulfide as a byproduct (Goldhaber and Kaplan, 1974; Berner, 1980; Rheinheimer, 1994). Hydrogen sulfide at contaminated sites may build up in sediments to concentrations thousands of times background levels (Gilmour et al., 2007b).

The excess sulfate and sulfide has numerous deleterious impacts on the Everglades. One of the more environmentally important impacts is the link between sulfate contamination and methylmercury (MeHg) production in the ecosystem (Gilmour et al., 1998; Benoit et al., 1998, 1999a, b; Axelrad et al., 2007; Gilmour et al., 2007a). MeHg, a bioaccumulative neurotoxin, is produced primarily by methylation of ambient inorganic mercury during MSR (Compeau and Bartha, 1985; Gilmour et al., 1992; Munthe et al., 1995; Branfireun et al., 1999). Contamination of fish with MeHg is the most significant environmental contaminant issue in the USA in terms of number of locations impacted (Krabbenhoft and Wiener, 1999; USEPA, 1998). Neurotoxic MeHg represents a serious threat to wildlife (Bouton et al., 1999; Frederick et al., 1999; Heath and Frederick, 2005), and is a human health issue, with human exposure through fish

consumption (Gilbert and Grant-Webster, 1995; Schober et al., 2003). In addition to its neurotoxic effects, MeHg may also be an endocrine disruptor that affects successful reproduction in fish and fish-eating wildlife (Klaper et al., 2006). South Florida has among the highest levels of MeHg in fish in the USA (Lambou et al., 1991). Experimental chamber (mesocosm) studies conducted in the Everglades have shown that sulfate addition stimulates the production and bioaccumulation of MeHg (Gilmour et al., 2007b). Inorganic mercury enters the Everglades primarily in rainfall, and most of the inorganic mercury in the rainfall appears to originate from outside of the USA (Hanisch, 1998). The origin of most inorganic mercury from outside of the USA severely limits the ability of state and Federal officials to limit MeHg production and bioaccumulation in fish in the Everglades by controlling emissions of inorganic mercury from various anthropogenic sources (e.g. coal-fired power plants, medical waste incinerators, cement manufacture). Thus, controlling sulfate inputs to the Everglades may represent the most effective way of minimizing MeHg production and bioaccumulation here.

In addition to impacts on MeHg production and bioaccumulation, sulfur contamination has also dramatically altered redox patterns in the Everglades. Unnaturally low (negative) redox and highly sulfidic conditions occur in large swaths of the northern Everglades heavily impacted by sulfate from canal discharge (Gilmour et al., 1997b). The lower redox conditions and high concentrations of toxic sulfide in soils may impact macrophytes and soil infauna (Koch et al., 1990; Bradley and Morris, 1990; Kludze and Delaune, 1996). A recent greenhouse study suggests that sawgrass (*Cladium*) is more sensitive to sulfide toxicity than cattail (*Typha*) at sulfide concentrations greater than 9 mg/L (Gilmour et al., 2007b). Sulfide concentrations exceeding 9 mg/L are routinely exceeded at heavily sulfate- and phosphorus-contaminated sites in the northern Everglades where cattail has displaced sawgrass. Various studies have suggested that excess phosphorus stimulates the growth of cattail over sawgrass in heavily impacted parts of the Everglades (Davis, 1991; Craft et al., 1995; Newman et al., 1996; Craft and Richardson, 1997; Miao and DeBusk, 1999; Childers et al., 2003). It is hypothesized, however, that sulfide buildup in soil also plays a key role in the displacement of sawgrass by cattail in the Everglades, probably in combination with phosphorus eutrophication (Gilmour et al., 2007b).

High levels of sulfide and low redox conditions may also impact trace metal cycling, and increase remobilization of nutrients from soils through a process referred to as internal eutrophication. Stimulation of MSR by excess sulfate has been shown to increase remobilization of nutrients from freshwater marshes in the Netherlands (Lamers et al., 1998; Smolders et al. 2006). Preliminary mesocosm studies have shown that sulfate can also enhance remobilization of ammonium, phosphorus, and dissolved organic carbon and nitrogen from Everglades' peats (Gilmour et al., 2007b). Thus, sulfate contamination of the Everglades may limit the ability of marsh soils to effectively sequester phosphorus contamination from EAA runoff.

Similarly, high levels of sulfate in stormwater treatment areas (STAs) will limit their ability to effectively sequester phosphorus from EAA runoff.

Current plans to decompartmentalize and restore sheet flow are likely to increase sulfate loads to areas such as Loxahatchee National Wildlife Refuge (LOX), Everglades National Park (ENP), and Big Cypress National Preserve (BCNP). Rerouting of water will impact different areas in different ways with some areas receiving greater sulfate loads and some areas receiving lower sulfate loads. In the central Everglades, recently reported declines of MeHg levels in fish appear to be linked to declines in sulfate concentration, not to declines in inorganic mercury deposition (Axelrad et al., 2007). In contrast, monitoring data suggest that sulfate-contaminated water has been rerouted down canals from the central Everglades to ENP, where recent increases in MeHg concentrations in fish have been reported (Gilmour et al., 2007a). Plans to move sulfate-contaminated water from the L-28 canal into BCNP may also result in increased MeHg levels in biota here. Elevated levels of MeHg in fish have been observed in the northeastern part of BCNP, in the area near the L-28 canal (D. Rumbold, personal communication). Other unwanted impacts of sulfate contamination may also occur in these areas. Unfortunately, STAs as currently designed do not significantly reduce sulfate loads discharged into the ecosystem (South Florida Water Management District, unpublished data). Land and water managers need to carefully assess the costs versus benefits of using sulfate-contaminated water in Everglades' restoration. Restoration efforts will not be considered successful if sulfidic soils and MeHg-contaminated fish persist in the ecosystem.

In this report we examine potential strategies for reducing sulfate loads to the Everglades (i.e. mitigation strategies). Any effort to mitigate sulfate loads to the Everglades might begin with considering reducing the principal sources of the contamination. This certainly would involve an evaluation of sulfur use in agriculture in the EAA (sugarcane and vegetable cultivation) and areas north of Lake Okeechobee (cattle and citrus) that drain into the lake and ultimately the Everglades. It may be possible to reduce sulfur use without seriously reducing crop yields. Alternatives to some soil amendments containing sulfur may be available, and unnecessary sulfur in some fertilizers or soil amendments could be eliminated by reformulation at the manufacturing level. This would require cooperation among agricultural scientists, the agricultural industry, fertilizer manufacturers, and government officials. Sulfate loads delivered to the Everglades will likely not be able to be reduced to pre-development levels. However, it cannot be emphasized too strongly that any reduction in sulfate load would benefit the ecosystem, especially with regard to the issue of MeHg production and bioaccumulation. Monitoring and mesocosm studies conducted in the central Everglades have shown how quickly MeHg production and bioaccumulation respond to reductions in sulfate loads.

In addition to reducing sulfate loads to the ecosystem, approaches for active reduction of sulfate concentrations in canal water are also considered. A number of approaches are presented, including

biological removal strategies, passive mineral removal, chemical treatment approaches, and active removal using various technologies. Many of these approaches will be impractical for removal of sulfate from Everglades' water due to scaling issues, cost, or other factors. The most effective approach to reducing sulfate loads to the Everglades will likely be multifaceted, involving reductions in sulfate sources, biological sequestration of sulfur, passive removal processes, and the use of already impacted marsh area to reduce sulfate loads to unimpacted parts of the ecosystem.

2. Review of Sulfur Contamination in the Everglades: Sources, Cycling, Sinks and Effects

2.1 Sulfur and microbial sulfate reduction - Sulfur is an important element in the biogeochemistry of wetland ecosystems because of its role (when present as sulfate) as a metabolic terminal electron acceptor in microbial sulfate reduction (MSR) (Goldhaber and Kaplan, 1974; Berner, 1980). In MSR, sulfate reducing bacteria (SRB) reduce sulfate to sulfide during the degradation (oxidation) of organic matter. A simplified chemical equation that describes MSR is:

$$2 \text{ CH}_2\text{O (organic carbon)} + \text{SO}_4^{2-} \text{ (sulfate)} \rightarrow \text{H}_2\text{S (sulfide)} + 2 \text{ HCO}_3^- \text{ (inorganic carbon)}.$$
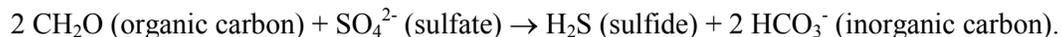
SRB are obligate anaerobes, and MSR occurs only under anoxic conditions, typically in wetland sediments (Rheinheimer, 1994). MSR plays an important role in wetland sediments through the degradation of organic matter, the recycling of nutrients, the regulation of redox conditions, and the control of metal concentrations (through formation of insoluble metal sulfides and redox control of metal solubilities). One of the most important environmental effects of MSR is the methylation of mercury by SRB. Methylmercury (MeHg) is a potent neurotoxin that bioaccumulates in fish and other wildlife. Toxic concentrations of MeHg in upper trophic level organisms are a serious environmental issue in many wetland ecosystems worldwide, including the Everglades. The presence of sulfate in wetlands is a key driver of mercury methylation.

    2.2 Sulfur contamination of the Everglades - Freshwater wetlands typically have low sulfur concentrations (Wetzel, 1975), but there is extensive sulfur contamination of the Florida Everglades (Orem, 2004). The extent of sulfur contamination in the Everglades has been documented by studies conducted by both the USGS and EPA (Orem et al. 1997; Stober et al., 2001; Bates et al., 2002). A recent EPA analysis shows that about 60% of the ecosystem has concentrations of sulfate in surface water above the 1 mg/L level considered to represent background (D. Scheidt and P. Kalla, EPA, personal communication). Sulfate (the major form of sulfur in surface water), like other contaminants entering the

ecosystem, tends to show a north-south concentration gradient in surface water, with higher concentrations in the north (Gilmour et al., 2007b). Sulfate concentrations in surface water of marshes of the northern Everglades average up to 60 mg/l, compared to <1 mg/l in pristine parts of the ecosystem located more than 10 km from the nearest canal discharge. This north-south gradient in water quality reflects the discharge of canal water with high concentrations of dissolved chemical constituents, including sulfate, into marshes in the northern part of the ecosystem. The canal water originates from Lake Okeechobee and rivers draining into the lake, and the canals also receive runoff from agricultural fields in the EAA. Contamination of the Everglades by phosphorus from canal water discharged into the ecosystem has been well documented (Koch and Reddy, 1992; Craft and Richardson, 1993; DeBusk et al. 1994). Contamination by other chemical species (e.g. sulfate), however, has only recently been acknowledged as a problem, and the effects of this contamination on the ecosystem are not fully known.

As excess sulfate enters the Everglades it stimulates MSR in the anoxic soils (peats) underlying the freshwater Everglades, producing toxic hydrogen sulfide as a byproduct. The sulfide builds up in pore water at sulfur-contaminated sites in the north to concentrations of 1,000s of ppb (up to 15,000 ppb), compared to sulfide concentrations below detection (<0.1 ppb) in pore water at pristine sites. There are also significantly higher levels of sedimentary sulfur, and higher sulfur accumulation rates in sediments at contaminated northern sites, compared to pristine areas (Gilmour 2007b).

2.3 Sources of sulfate contamination – Historically, the freshwater Everglades likely received most of its sulfate input from overflow runoff from Lake Okeechobee, and from rainfall. There is no evidence that groundwater played a significant role in sulfate supply to the Everglades, as porewater profiles from throughout the ecosystem show no increase in sulfate near the soil/bedrock interface. Pristine areas of the Everglades today probably receive most of their sulfate input from rainfall because overflow from Lake Okeechobee has been shut off by construction of canals and compartmentalization of the ecosystem.

In contrast to pristine areas, sulfur-contaminated areas of the ecosystem appear to receive most of their sulfur input as sulfate in surface water from canal discharge. The highest levels of sulfate within the entire south Florida ecosystem are observed in canal water within the EAA, based on studies conducted by both the EPA and USGS. Average sulfate concentrations in surface water along a transect proceeding from Lake Okeechobee in the north to sites in the Everglades marshes to the south shows: (1) an increase in average sulfate concentrations from the lake to canals within the EAA, (2) peak average concentrations of sulfate in canal water within the EAA, and a gradual decrease in average sulfate concentrations proceeding south and east along the canals, and (3) decreasing average sulfate concentrations in Everglades' marshes with increasing distance from canal discharge points. Thus, the surface water sulfate concentration data suggest that the principal source of excess sulfate entering the Everglades originates

from canal water within the EAA. Average concentrations of sulfate in Lake Okeechobee (about 25 mg/L) are significant, but much lower than average sulfate concentrations in EAA canals (60-70 mg/L). Backpumping of canal water directly into Lake Okeechobee or into the canal rimming the lake, leakage from the rim canal, and runoff of high sulfate water from EAA soils into Lake Okeechobee may contribute to the relatively high levels of sulfate in surface water of the lake.

The source of the sulfate to the canals, however, is a more controversial topic, and certainly worthy of further work. Stable isotopic analysis (δ^{34}S) of sulfate in surface water from marsh sites and canals was conducted by the USGS to examine the sources of the sulfate (Bates et al., 2001, 2002). The use of sulfur isotope geochemistry for source studies is complicated by fractionation during MSR where the isotopically lighter sulfate is preferentially reduced to sulfide by SRB leaving the remaining sulfate isotopically heavier (Thode et al., 1961; Nakai and Jensen, 1964). Nevertheless, because this fractionation occurs in a predictable direction, plotting sulfate concentration versus the sulfur isotopic composition (δ^{34}S) of sulfate can provide insight into the source(s) of sulfate. Results (Bates et al. 2002) show a relatively wide spread of δ^{34}S values at low sulfate concentration, reflecting the different sources and redox changes that can contribute to the sulfate pool at pristine sites with low sulfate concentrations (typically < 1mg/L). As sulfate concentration increases, the spread of δ^{34}S values decreases, and a distinct trend line is apparent in the data indicating that a single source of sulfate begins to dominate as sulfate concentrations increase. The very highest sulfate concentrations observed in canal water within the EAA approach a δ^{34}S value of about +16 ‰, suggesting the isotope ratio value of the source of the sulfur.

Because of the known phosphorus contamination of the Everglades due to agricultural runoff from the EAA (Koch and Reddy, 1992; Craft and Richardson, 1993; DeBusk et al., 1994; Zielinski et al., 1999) and the extensive use of sulfur in agriculture in the EAA (Bottcher and Izuno, 1994), USGS scientists hypothesized that the source of sulfate in EAA canals may originate from agricultural applications on EAA fields. Agricultural sulfur (a form of elemental sulfur that is 98% S^o) is used as a soil amendment and fungicide in the EAA (Bottcher and Izuno, 1994). Sulfur isotopic analyses [δ^{34}S] of agricultural sulfur from the EAA had a range of δ^{34}S values (15-20‰) that were consistent with agricultural sulfur as a major source of the sulfate in EAA canals. Also, sulfate extracted from the upper 10 cm of soil in an active sugarcane field in the EAA had a δ^{34}S value of 15.6 ‰ (Bates et al., 2001 and 2002) suggesting contamination from agricultural sulfur. From these data, USGS scientists have hyopthesized that the agricultural sulfur applied in the EAA is: (1) oxidized to sulfate in the largely aerobic soils (through the action of sulfur oxidizing bacteria), (2) remobilized from the soils by rainfall and/or irrigation, (3) transported as sulfate in runoff to the canals in the EAA, and (4) discharged to the Everglades in canal water. Note that the isotopic data [δ^{34}S] do not indicate whether the sulfate entering the canals in the EAA

is derived from recently applied agricultural sulfur, historical applications slowly released during soil oxidation, or potentially both.

Another approach to determining the source(s) of sulfate to EAA canals is to examine all possible sources (Fig. 1). USGS studies (Bates et al., 2002; Gilmour et al., 2007b) of different sulfate sources have shown the following: (1) Rainwater has sulfate concentrations that are too low to account for the amount of sulfate in EAA canals, and it has a sulfur isotopic composition [$\delta^{34}S$] much lighter (+2 to +6‰) than that of canal water (+15 to +23‰). (2) Lake Okeechobee certainly contributes to the sulfate observed in EAA canals, but has sulfate concentrations nearly 3 times lower than those in the canals. Lake Okeechobee may receive much of its sulfate from EAA canals through backpumping and leakage from the rim canal. Thus, Lake Okeechobee becomes essentially a part of the canal system from the standpoint of sources of sulfate. (3) Groundwater may also contribute sulfate to the ecosystem; however, studies of
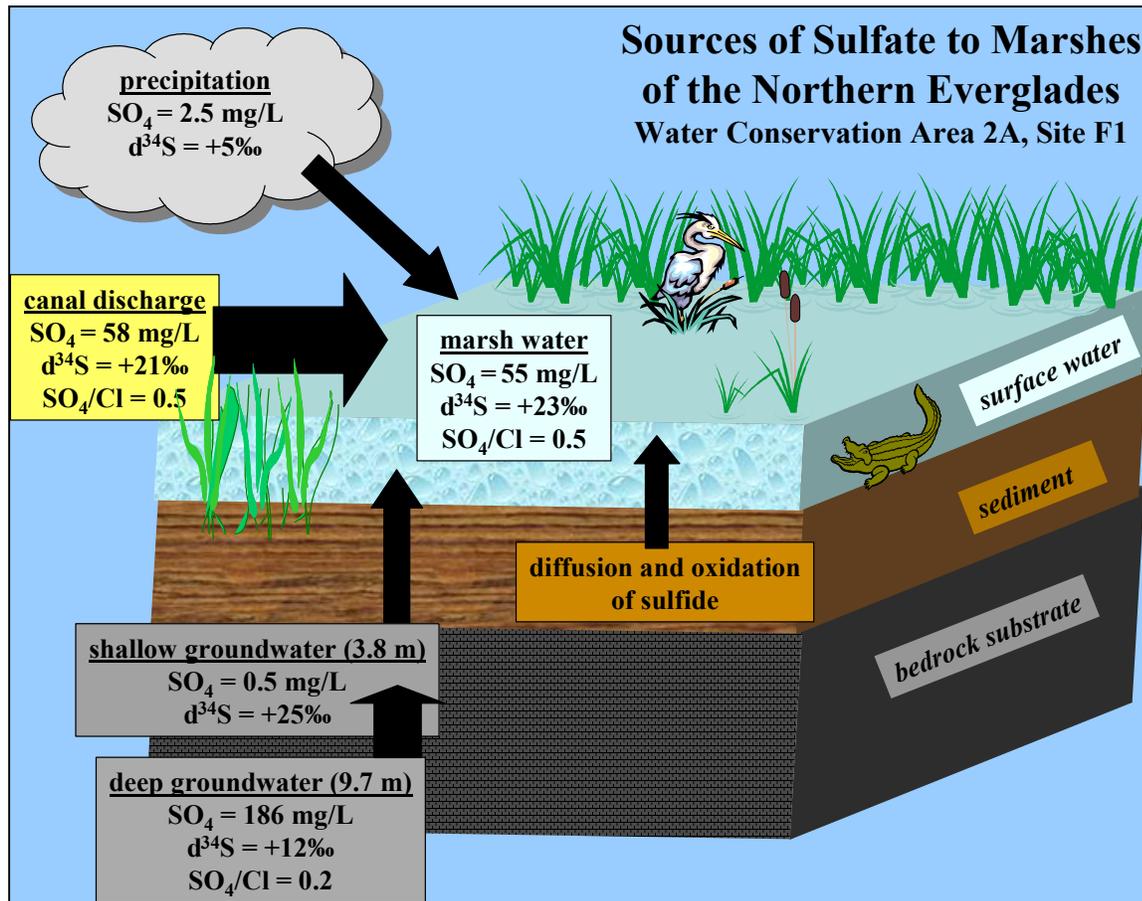
Fig. 1. Sources of sulfate to a marsh site in Water Conservation Area 2A. Boxes show the sulfate concentration (mg/L), the isotopic composition of sulfate S ($\delta^{34}S$), and the sulfate/chloride ratio of different water sources considered (precipitation, canal discharge, groundwater). Results point to canal discharge from the EAA as the major source of sulfate to this marsh site.

potential groundwater sources are rather limited at present. The available data show that shallow groundwater (<9 m) has relatively low sulfate and could not be a major source of sulfate, but deep groundwater (>9 m) has very high sulfate levels and is potentially a major sulfate source. Deep groundwater, however, has a sulfur isotopic composition ($\delta^{34}S$), sulfate/chloride values, and a uranium composition significantly different from that in surface water (Zielinski et al., 1999; Bates et al., 2002; Axelrad et al., 2007; Gilmour et al., 2007b). Thus, the available dataset, though limited, suggests that deep groundwater is not a major contributor to the sulfate found in surface waters of the canals or marshes of the Everglades. This leaves agricultural sources of sulfur (current and legacy) in the soil of the EAA as the most likely major source of sulfate contamination to the ecosystem, based on currently available information.

2.4 Fate of sulfur in the ecosystem - The principal sink for sulfur in the ecosystem is long-term storage in sediments (Fig. 2). Sequestration of sulfur in sediments typically results from microbial reduction of
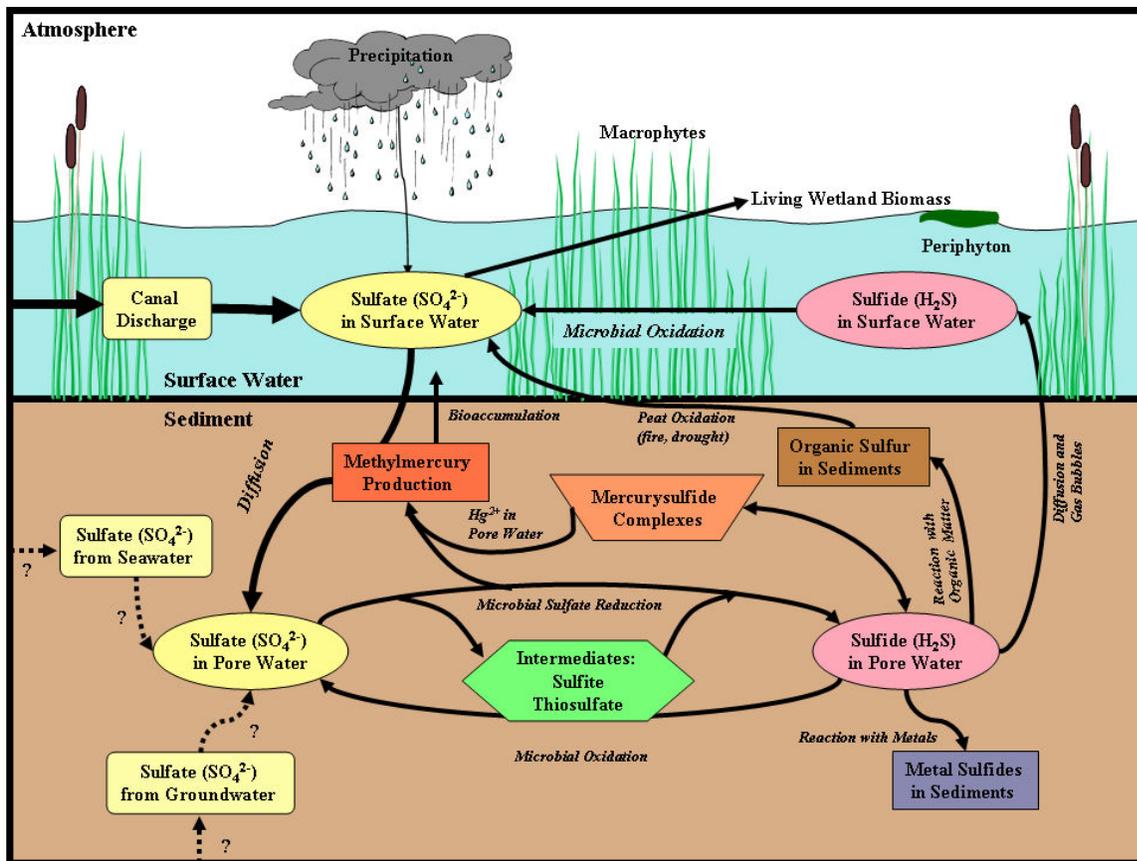
Fig. 2. Simplified sulfur cycle for the freshwater Everglades. Seawater may contribute sulfate at some locations near the coast. Groundwater is not known to contribute sulfate to Everglades' pore water.

sulfate to sulfide, and subsequent reaction of sulfide with organic matter to form organic sulfur compounds, or reaction with metals to form insoluble metal mono- and disulfides. The sequestration of sulfur in sediments, therefore, is dependent on a number of factors, including: redox conditions, the load of sulfate available for SR, the amount of organic matter available for reaction to form organic sulfur species, and the concentrations of dissolved metal ions available for formation of metal sulfides. Florida Bay, for example, has high surface water sulfate concentrations (up to 3,000 mg/L) and porewater sulfide concentrations (up to 100 mg/L), but relatively low sulfur concentrations in sediments (generally <0.3%; W.H. Orem, unpublished data). The low organic matter and metal content of sediments from Florida Bay limit the amount of sulfur sequestered. Sediments in the Everglades with high mineral matter content (usually composed of low sulfur quartz sand and carbonates) have lower sulfur concentrations, compared to peats with their high organic matter content.

Sulfur speciation analyses show that most of the sulfur in sediments from the freshwater Everglades is in the form of organic sulfur (Bates et al., 1998). Organic sulfur accounts for 50-85% of the total sulfur at most sites (Fig. 3). Some of this organic sulfur originated from the living biomass that formed the peat underlying the Everglades, but a larger fraction of the organic sulfur likely formed by the reaction of sulfide with organic matter (Casagrande et al., 1976 and 1979; Casagrande and Ng, 1979). Disulfides (e.g. pyrite) and sulfates were the next most abundant sulfur species in these sediments. Disulfides generally accounted for 10-30% of the total sulfur, and sulfates range from 5-30% of the total sulfur. Acid volatile sulfides (monosulfides) represent only a small fraction of the total sulfur in the sediments, ranging from 0-2% and generally <1%. This is probably due to iron limitation of monosulfide fixation.

Accumulation rates for sulfur in surface sediments (g m^{-2} day^{-1}) from selected freshwater marsh sites in WCA 1, 2, and 3, and ENP, and for two sites from a brackish water mangrove swamp in ENP ranged from 9.0×10^{-3} to 0.38×10^{-3}, a more than 20 fold difference. The highest sulfur accumulation rates were observed at the brackish water mangrove sites and in the sulfur-contaminated freshwater marsh sites. Average sulfur accumulation rates for four pristine sites, four sulfur-contaminated sites, and two mangrove sites (brackish water) were 1.6×10^{-3}, 4.5×10^{-3}, and 6.0×10^{-3} g m^{-2} day^{-1}, respectively. Thus, areas in the freshwater Everglades receiving excess sulfur from canal discharge are accumulating (on average) nearly three times as much sulfur in the sediments as pristine freshwater sites, and approach values found in brackish water mangrove areas (W. H. Orem, unpublished data).

The sequestered organic sulfur and metal sulfide chemical species in sediments are relatively stable under anoxic conditions. Oxidation of the sediment, however, from drought or fire can result in the sequestered sulfur being reoxidized to sulfate and remobilized by subsequent reflooding. In May and June 1999 drought and fire affected a large percentage of WCA 3 north of Alligator Alley (Interstate 75; see
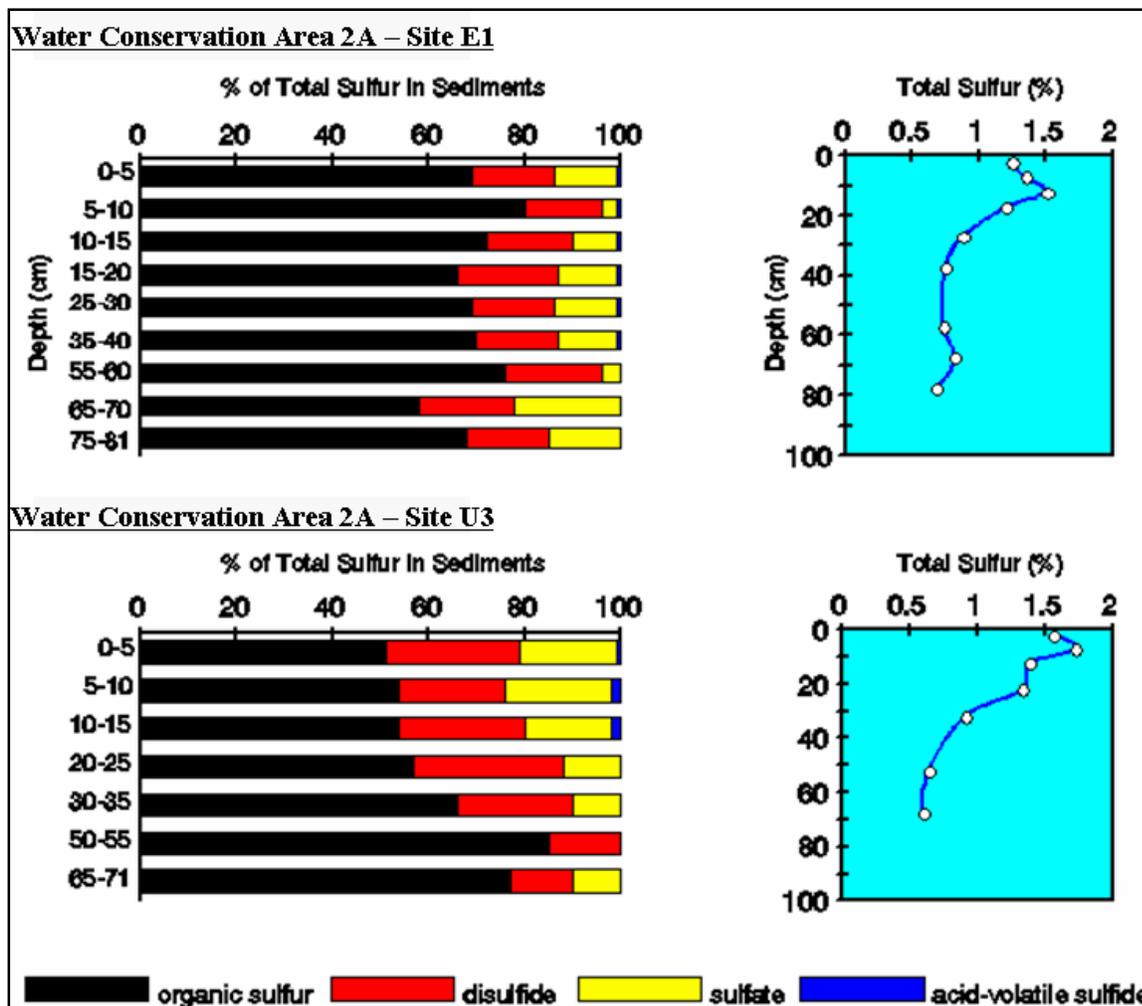
Fig. 3. Total sulfur content with depth and sulfur speciation in soils from two sites in Water Conservation Area 2A.

Fig. 6). Following the fire and reflooding of this portion of the Everglades, samples of surface water, porewater, and sediment were collected for sulfur studies. Prior to the burn, surface water sulfate concentrations in this area averaged 7 mg/l, but one month after the burn, surface water sulfate levels at 14 sites in the burned area averaged 58 mg/l (W.H. Orem, unpublished data). This eight fold increase in sulfate concentrations stimulated MSR, and resulted in a significant increase in mercury methylation two months after the burn (D. P. Krabbenhoft, USGS, personal communication). Thus, seasonal drought/fire and rewetting of Everglades peats play a key role in sulfur cycling, MSR, and episodes of high methylmercury production in the ecosystem.

2.5 Impacts of sulfate contamination - The major known impact of S contamination on the Everglades is its link to methylmercury (MeHg) production (Gilmour et al., 1998; Axelrad et al., 2007). MeHg is produced from Hg (II) by SRB (Compeau and Bartha, 1985). Sulfate stimulates SRB activity and MeHg production, but buildup of sulfide in sediment porewater inhibits MeHg production (Gilmour et al., 1992; Benoit et al., 1999a and b). This dual effect of S on MeHg production produces maximum MeHg concentrations in areas of the Everglades with intermediate S contamination, so-called "Goldilocks Areas" where sulfate and sulfide levels are just right for mercury methylation. This conceptual model for the role of sulfate in MeHg production has been verified for the Everglades by field, laboratory, and mesocosm experiments, and likely applies in most freshwater wetlands (Munthe et al., 1995; Branfireun et al., 1999). A different model may apply to mercury methylation in the marine environment (Benoit et al., 1998).

The Everglades has a unique set of conditions for producing high levels of methylmercury in fish and other wildlife. Conditions promoting the methylation of mercury and its bioaccumulation in Everglades biota include: (1) high rates of mercury deposition (mostly from long-range atmospheric transport), (2) a large wetland area, with nominally anoxic soils (peat) that are ideal for microbial methylation of mercury, (3) high levels of dissolved organic carbon (DOC) in the water column, which complexes and stabilizes the dissolved mercury (Hg^{2+}), helps in transport of the dissolved mercury to sites of methylation, makes it more bioavailable for methylation, and may assist in transport of MeHg for bioaccumulation, (4) high levels of sulfate (from agricultural contamination and possibly other sources), which stimulate microbial sulfate reduction and mercury methylation, and (5) effective trophic level transfer of MeHg from the site of production (in the soil) into the food chain. The high level of MeHg produced and bioaccumulated in the Everglades poses a threat to fish and fish-eating wildlife through endocrine disruption and neurotoxicity (Heath and Frederick, 2005), and poses a health threat to humans through fish consumption. Especially at risk from neurotoxicity are the unborn and developing young of wildlife, and human fetuses. Declines in reproductive success related to high levels of MeHg may be one factor contributing to declines in wading birds in the Everglades over the past century (Bouton et al., 1999; Frederick et al., 1999). With respect to human health, about 8% of women in the USA of child-bearing age have blood levels of methylmercury that could be dangerous to a developing fetus (Schober et al., 2003). Neurotoxic effects on developing fetuses include cerebral palsy and mental retardation at high levels of MeHg exposure. Low birth weight and sensorimotor dysfunction such as delayed walking are other effects (Gilbert and Grant-Webster, 1995).

Another important feature of the S-MeHg connection in the ecosystem is the stimulation of MeHg production by fire/drought and subsequent rewet of wetland areas (Krannenhoft and Fink, 2001). Fire/drought results in: (1) oxidation of organic soils, transforming reduced S in sediments to sulfate, (2)

remobilization of this sulfate following rewetting, and (3) stimulation of MeHg production by the remobilized sulfate. The fire/drought model linking S and MeHg production has important implications for management of the Everglades and Stormwater Treatment Areas (STAs). The effects of fire/drought and subsequent rewet on sulfate remobilization from soils and subsequent stimulation of mercury methylation have been verified in both field and laboratory microcosm studies (Gilmour et al., 2007 a,b).

In order to reduce the amounts of MeHg produced and bioaccumulated in the Everglades, the factors promoting methylation need to be altered. Reductions in the amount of wetland present are obviously not appropriate with respect to restoration goals, although minimizing the occurrence of dry/rewet cycles would reduce spikes in MeHg production. Reducing DOC could reduce the bioavailability of Hg^{2+} for methylation, but reducing DOC would be virtually impossible in a peat-forming environment like the Everglades. Because most mercury deposited on the Everglades is apparently from long-range atmospheric transport (outside the USA), control of local or even national emissions will have limited impact on the mercury problem here. Control of sulfate inputs, essentially reducing the capacity of the ecosystem to support MSR and mercury methylation, is currently being explored as the principal tool for reducing MeHg production and bioaccumulation in the Everglades.

In addition to its role in the MeHg problem in the Everglades, sulfate contamination may have other unintended consequences. Increased external sulfate loading to wetland soils has been demonstrated to lead to enhanced mobilization of N and P from soils. This process is referred to as internal eutrophication, or eutrophication of wetland surface waters as a result of changes in water quality without additional external supply of nutrients (Lamers et al., 1998; Smolders et al., 2006). Alkalinity and sulfate are the water quality parameters most often producing internal eutrophication. Sulfate-mediated internal eutrophication occurs as excess sulfate loading stimulates MSR and buildup of sulfide in flocs and soils. The excess sulfide drives down the redox potential of these zones, releasing redox-sensitive nutrient species (ammonium and phosphate) from the soils. Increased MSR also generates excess alkalinity, further enhancing phosphate and ammonium remobilization (Smolders et al. 2006). Mesocosm studies conducted in the central Everglades have shown that there is a significant release of ammonium and phosphate from soils to pore water and surface water following dosing with sulfate at concentrations of 20-100 mg/L (similar to concentrations found at heavily sulfate-impacted sites in the northern Everglades). The added sulfate stimulates MSR in surface soil in the mesocosms, with buildup of sulfide and lowered redox conditions (Orem et al., 1997). Thus sulfate entering the ecosystem may be exacerbating the phosphorus contamination problem in the Everglades by enhancing remobilization of sequestered phosphorus from the soil. High levels of sulfate in the STAs will also limit their ability to effectively sequester phosphorus in peat.

Sulfate-reducing bacteria are metabolically more versatile than methanogenic bacteria. Thus, sulfate addition to freshwater wetlands may increase overall organic carbon utilization and reduce the rate of carbon (e.g. peat) sequestration in soils. Preliminary results from sulfate addition mesocosm studies conducted in the central Everglades show increased remobilization of DOC and total dissolved nitrogen (including organic nitrogen compounds) with increased sulfate loading.

Buildup of sulfide in Everglades soils resulting from sulfate contamination also presents a problem of direct toxicity to wetland plants and other organisms, especially those adapted to freshwater (e.g. low sulfate and sulfide) conditions. Sulfide buildup drastically reduces wetland soil redox conditions (Gilmour et al., 2007b), which may inhibit the availability of oxygen for rooted macrophytes and soil infauna. Sulfide is toxic to wetland macrophytes through the inhibition of enzymes involved in anoxic energy production in root cells (Koch et al., 1990). Sulfide may also inhibit nutrient uptake in wetland macrophytes (Bradley and Morris, 1990). Recent work by I. Mendelssohn from Louisiana State University (reported in Gilmour et al., 2007b) has shown that sawgrass (Cladium) is more sensitive to the toxic effects of sulfide compared to cattail (Typha), especially at sulfide concentrations above 9 ppm. Sulfide concentrations exceeding 9 ppm have been observed at sites in the northern Everglades, especially at locations with high sulfate loading near canal discharge where cattails have replaced sawgrass as the dominant macrophyte (Gilmour et al., 2007b). The prevailing theory for explaining the invasion of cattail and displacement of sawgrass in the northern Everglades has been eutrophication due to phosphorus runoff from the EAA (Davis, 1991; Craft et al., 1995; Newman et al., 1996; Craft and Richardson, 1997; Miao and DeBusk, 1999; Childers et al., 2003). Could sulfur also play a role in facilitating the displacement of sulfide-sensitive sawgrass by sulfide-tolerant cattail? Further work is needed to explore this question; however, there is no doubt that sulfate contamination has had and is having a profound impact on the ecosystem. The question then becomes, what can be done to reduce levels of sulfate entering the Everglades?

3. Reducing the Source(s) of Sulfate to the Everglades

3.1 Sulfur use in agriculture - Sulfur plays three principal roles in agriculture: (1) as a plant nutrient, (2) as a soil amendment for pH adjustment, and (3) use as a fungicide (Meyer, 1977). Sulfur is also present in a number of fertilizers where it serves the purpose of an additional plant nutrient and as a counter ion to the principal nutrient in the fertilizer (Table 1). Sulfur (as sulfuric acid) is also used in the production of phosphate fertilizer from phosphate rock, with phosphogypsum produced as a byproduct (Ober, 1999). Only a small amount of phosphogypsum is used as a soil amendment in agriculture because of its high

Table 1. Sulfur content (dry wt.) of various agricultural chemical applications.

Application Material	%S
Ammonium Sulfate	24
Ammonium Thiosulfate	26
Calcium Sulfate (gypsum)	15-18
Magnesium Sulfate	23
Potassium-Magnesium Sulfate	28
Potassium Sulfate	18
Superphosphate	12
Aluminum Sulfate	14
Copper Sulfate	13
Manganese Sulfate	14-17
Zinc Sulfate	13-18

radium content (derived from the phosphate rock). More than 700 million tons of phosphogypsum is stored in large piles in central Florida, where it poses a hazard to surface and groundwater (Johnson and Traub, 1996).

Sulfur is a basic nutrient requirement for plant life including agricultural plants such as sugarcane and vegetables grown in the EAA, citrus trees cultivated north of Lake Okeechobee, and grasses used by cattle north of the lake (Fig. 4). Indeed, sulfur is required in about the same amounts as phosphorus by plants (Beaton, 1966; Tabatabai, 1984). Plants utilize sulfur for the synthesis of essential amino acid and proteins, some vitamins and coenzymes, glycoside oils, disulfide linkages and sulfhydryl groups, and for enzyme activation (Coleman, 1966). The molar sulfur/nitrogen ratio (a measure of plant sulfur requirements) ranges from about 0.02 to 0.03, which is about the same as the molar S/N ratio in plant proteins that constitute about 80 per cent of the organic S and N present (Dijkshoorn and Van Wijk, 1967). For sugarcane, sulfur requirements in the plant vary with age from 0.36% (whole plant) and 0.24% (leaf blades) for early growth, to 0.10% (leaf blades) and 0.08% (leaf sheaths) in 70 day old plants (Fox, 1976). Sulfur for plant nutrition can be applied directly as elemental sulfur, sulfur-bentonite mixes, ammonium sulfate, potassium sulfate, or superphosphates. Decreases in atmospherically deposited sulfur from air pollution in recent years may increase the need for sulfur fertilization of crops in some locations (Donald et al., 1999).

As a soil amendment, agricultural sulfur is used to adjust soil pH (Boswell and Friesen, 1993). The pH of soil can affect the uptake of essential nutrients by sugarcane and other agricultural plants. For example, at a pH of 7.5 or higher, virtually all phosphorus will be tied up as calcium phosphate and unavailable for plant growth. Other nutrients (e.g. potassium and nitrogen) also become less available for
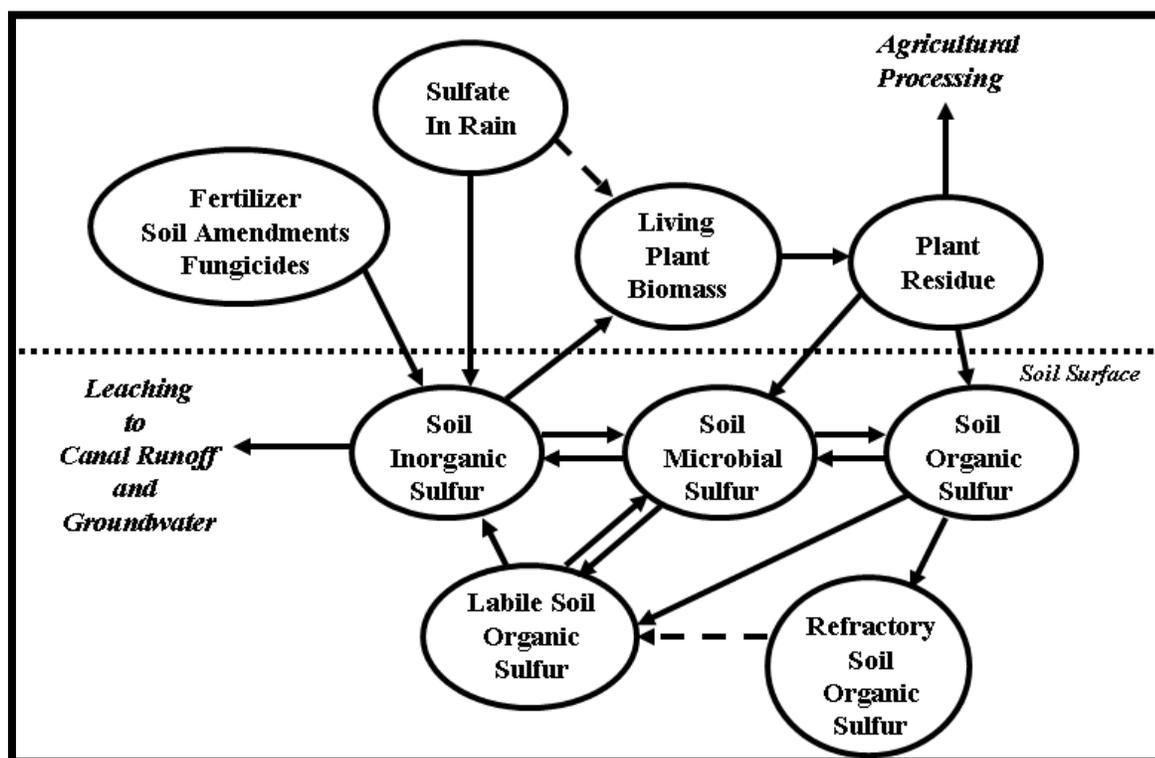
Fig. 4. Hypothetical sulfur cycle for EAA soils.

supporting plant growth at higher pH. The optimum pH for uptake of most nutrients is about 6.5. To adjust pH to optimum values for nutrient uptake by plants, elemental sulfur (agricultural sulfur) is often added to the soil. In oxic soils (such as surface soils in the EAA) the elemental sulfur is oxidized to sulfuric acid (S + 3/2 O_2 + H_2O → H_2SO_4), with the process usually catalyzed by aerobic bacteria (e.g. Thiobacillus sp.). The rate of acid release from elemental sulfur can be controlled by the size of the sulfur particles added. Agricultural sulfur has historically been added to EAA soils, and continues to be used as a soil amendment in the EAA. Gypsum may also be added to soil to increase the sulfur content and as a soil amendment. Sulfate derived from both elemental sulfur oxidation and from gypsum has been shown to be highly mobile in organic matter-rich soils (Rhue and Kamprath, 1973). Gypsum or agricultural sulfur applied to soil in the EAA may be readily leached into drainage canals as sulfate. In contrast, Sakadevan and others (1993) found sulfur applied as fertilizer (superphosphate) to grazing fields was stored in the soil mostly as organic sulfur, and released as sulfate primarily through mineralization of the soil organic matter rather than directly from the fertilizer.

Elemental sulfur is also among the oldest fungicides still in use. Sulfur and copper-containing mixtures were the major fungicides used in agriculture until the advent of synthetic organic compounds (e.g. alkyldithiocarbamates, organotins, quinones, and phthalimides) in the 1940s. In the 1960s systemic

materials with more specificity for individual fungal organisms were developed (Wheeler, 2002). Bacterial fungicides, bacteria that compete with and attack specific fungi, have recently been developed as a potential alternative to chemical fungicides (National Academy of Sciences, 2000). These bacterial fungicides are not widely used yet, but offer a potentially more environmentally friendly alternative to chemical fungicides in the future. Natural chemicals produced by bacteria, plants, and other organisms are another focus of study for environmentally safe fungicides. For example, a number of substances isolated from Bacillus bacteria have been shown to control some significant fungal diseases of corn, potatoes, and beans (National Academy of Science, 2000). These natural substances offer a wide variety of active chemical ingredients with new mechanisms of antifungal action, and they have low risks to the environment. Sulfur and sulfur-containing compounds, however, are still used extensively as broad-spectrum fungicides at rates of 100 tons/yr for vegetable growing areas and 583 tons/yr for citrus growing areas within the South Florida Water Management District management area (Miles and Pfeuffer, 1997). Copper sulfate is another sulfur-containing fungicide still widely used in citrus production (Michaud and Grant, 2003; McCoy et al., 2003). Methyl bromide (3064 tons/yr) and chloropicrin (374 Tons/yr) are probably the most important fungicides used in the EAA, mostly on vegetable crops (Miles and Pfeuffer, 1997).

The amount of total sulfur used in various soil amendments, fertilizers, and fungicides in the EAA is unknown. Also unknown is the total sulfate entering canals as runoff from EAA fields. The EAA soils in general have pH values ranging from about 5 to 7.5, and possibly higher than 7.5 in some cultivated fields (Bottcher and Izuno, 1994). Ideal pH for phosphorus uptake from soil by crops is about 6, while many metal micronutrients are taken up most efficiently at pH <6 (Lucas, 1982). Thus, for most efficient uptake of phosphorus and metals, the pH of soil in the EAA are often reduced. This is typically accomplished by the addition of elemental sulfur (agricultural sulfur), as discussed earlier.

Schueneman and Sanchez (1994) indicate that elemental sulfur in the amount of 500 to 1,700 kg/ha-yr is needed to reduce the pH of soil by 0.2 to 0.7 units for vegetables in the EAA, and 560 kg/ha-yr for multiyear sugarcane production. In a later publication, Schueneman (2000) suggests that about 37 kg/ha-yr of sulfur (about 111 kg/ha-yr converted from sulfur to sulfate) is currently added to EAA soil, based on interviews with farmers in the EAA and estimates from fertilizer sales. This estimated total includes sulfur additions to EAA soil from agricultural sulfur and superphosphate, but does not include additions of other fertilizers (Table 1), nor does it include fungicides containing sulfur. Schueneman (2000) also incorrectly estimates contributions from Lake Okeechobee by a factor of 3 due to a calculation error. Schueneman (2000) also assumes none of the sulfate in Lake Okeechobee originates from sulfur use in the EAA, an unlikely assumption considering the high sulfate levels in the EAA rim canal adjacent to the lake. Lake Okeechobee also receives some sulfate contributions from sources north of the lake, but the

source is unclear at this time (Zielinski et al., 2006). The release (as sulfate) of sulfur sequestered in soil in the EAA as a result of soil oxidation is the largest single contributor to sulfate in EAA canals in the estimate of sulfur sources by Schueneman (2000). The sulfate released following soil oxidation likely includes current and legacy sulfur used for agriculture within the EAA as well as some natural (background) sulfur. Soil sulfur levels in the EAA are considerably higher than those of the nearby Everglades, indicating anthropogenic contributions to soil total sulfur. Thus, the conclusion in Schueneman (2000) that most of the sulfur entering canals in the EAA is from "natural" sources is misleading. Evidence that the high sulfate levels in canal water within the EAA originates largely from agricultural sources of sulfur was discussed earlier (also, see Bates et al., 2002).

Understanding where sulfur in EAA canals originates is critical for developing strategies for eliminating or reducing the source(s). Mass balance studies of the total sulfur used yearly in agricultural lands and urban areas, and sulfate runoff from EAA lands would constrain these anthropogenic sources. Additional studies of the contribution (if any) of deep groundwater to sulfate loads in EAA canals would also provide important information to managers (see section 3.2). Based on the current data, it is reasonable to assume that current agricultural practices (fertilizers, soil amendments, fungicides) introduce some of the sulfate entering canals in the EAA. Any reduction in sulfate load is likely to benefit the ecosystem's health. Reductions in the amount of sulfur used in agriculture will be necessary to achieve any significant reductions in sulfate loads to the ecosystem. Reducing the use of sulfur in the EAA will only be accomplished by involving all stakeholders in determining ways to balance the sulfur needs of agriculture with minimizing sulfur loading to the Everglades. Fertilizer manufacturers could consider the use of chloride instead of sulfate as the counter ion in many fertilizers. Unfortunately, the sulfur and phosphorus contamination issues are in conflict because reducing phosphorus use encourages use of sulfur to make more phosphorus available to crops. Best management practices (BMPs) in the EAA will need to incorporate considerations for the use of both sulfur and phosphorus in agriculture, but will need to balance profitability for farmers with protection of the environment.

3.2 Sulfate in groundwater – Groundwater in the Everglades has variable sulfate contents. In general, groundwater < 9m below the surface often has relatively low sulfate concentrations, generally < 10 mg/L, while groundwater deeper than 9 m may have sulfate concentrations ranging from 100s to 1,000s of mg/L, probably representing connate seawater (Sprinkle, 1989; Bates et al., 2001). These very high sulfate and total dissolved solids levels in deep groundwater show that deep groundwater could be a significant contributor to sulfate contamination of canals and Everglades' wetlands. The available dataset, however, does not support deep groundwater as a major source of sulfate to the ecosystem (Gilmour et al.,

2007b). Further work is needed to examine the role (if any) of groundwater as a source of sulfate contamination to the ecosystem.

If groundwater does contribute to sulfate loads to the Everglades ecosystem, this most likely occurs from advection of groundwater through the fractured bottoms of canals or via direct pumping of groundwater for fire control or other purposes. Studies of porewater from soil profiles to bedrock throughout the Everglades provide no indications of significant groundwater flux (advection or diffusion) of sulfate through marsh soil (Orem, unpublished data). Reduction of any groundwater pumping released to the canals (directly or indirectly) could be considered. Sealing of canal bottoms (a potentially expensive undertaking) could solve problems of advection of high sulfate groundwater.

3.3 Water from aquifer storage and recovery - One part of the Comprehensive Everglades Restoration Plan (CERP) calls for storage of surface water in underground aquifers for later removal, so-called aquifer storage and recovery (ASR) (National Research Council, 2002). Water accumulated during wetter periods would be stored in underground aquifers for later removal during drier periods. The principal storage reservoir planned for use in south Florida under CERP is the Upper Floridan aquifer. Unfortunately, in south Florida this aquifer contains brackish to saline water that may affect the quality of the surface water collected and stored for later use (Reese, 2001). Sulfate concentrations in the Upper Floridan aquifer generally range from 100 – 1,000 mg/L (Reese, 2000; Reese and Memberg, 2000), which is similar to values observed in groundwater > 9 m deep as reported by Bates and others (2002). Mixing of the high sulfate groundwater in the aquifer with lower sulfate in the stored freshwater will increase sulfate levels in the recovered water (Fig. 5). In addition, surface freshwater stored in the Upper Floridan aquifer may acquire sulfate from dissolution of gypsum in the aquifer matrix (Reese, 2000; Wicks and Herman, 1996). Sulfate could be lost from water stored in an ASR system if MSR causes precipitation of sulfide minerals or other forms of sulfide sequestration.

Preliminary studies of ASR water quality in south Florida (Mirecki, 2004) indicate that sulfate concentrations in recovered water do not exceed the 250 mg/L standard for drinking water supplies (Code of Federal Regulations, 2002). The 250 mg/L level, however, is far in excess of sulfate concentrations in surface water of marshes and canals in the freshwater Everglades (Bates et al., 2002). This indicates that the surface water stored in the Upper Floridan aquifer has acquired a significant load of sulfate during short term storage. Discharge of ASR water into the ecosystem will therefore increase sulfate loading. The drinking water standard is based on human health effects (gastrointestinal issues) from drinking high sulfate water, and does not take into account the adverse impacts on the ecosystem of sulfide and MeHg production from MSR stimulated by the excess sulfate. It is important to consider the use of ASR water in terms of costs (lower water quality) and benefits (more water) to the ecosystem. Mitigation

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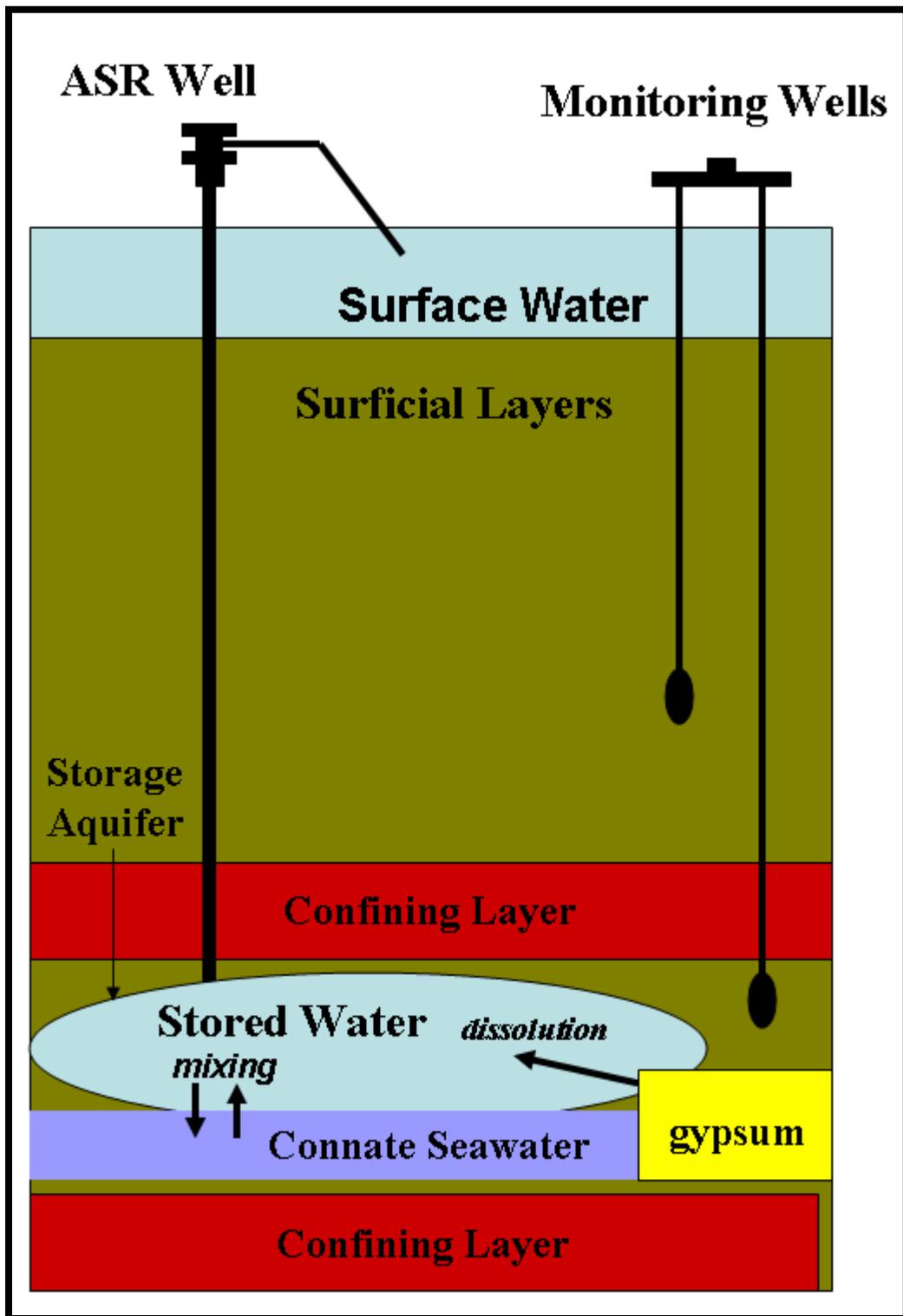
Fig. 5. Schematic of an aquifer storage and recovery (ASR) well in south Florida, illustrating how sulfate levels in stored water may be elevated through mixing with connate seawater and dissolution of gypsum minerals in the storage aquifer.

of sulfate in ASR water will likely be needed to avoid excessive sulfur contamination of the Everglades and resulting impacts, such as MeHg production and bioaccumulation, sulfide toxicity to biota, and enhanced N and P remobilization, that would be detrimental to the ecosystem.

3.4 Flow path – One of the major goals of Everglades' restoration is the movement of more water to areas to the south, especially Everglades National Park (ENP) (Perry, 2004; U.S. Army Corps of Engineers, 1996; U.S. Army Corps of Engineers and South Florida Water Management District, 1999). Ultimately, planners hope to achieve sheet flow across the current Water Conservation Areas and into ENP, simulating the flow of water in the ecosystem prior to development and water management beginning in the early 1900s (Clarke and Dalrymple, 2003).

From the standpoint of reduction of sulfate contamination across the ecosystem, sheet flow is probably the most desirable option. Slow sheet flow across a wetland will allow effective diffusion of sulfate into Everglades' soil (peat) where MSR and sequestration of the resulting sulfide can occur. Moving sulfate-contaminated canal water through re-engineered STAs or PASTAs, and then by slow sheet flow across the northern Water Conservation Areas may prove an effective treatment for protecting the more unimpacted parts of the Everglades further south. A less desirable option is the directed flow of sulfate-contaminated canal water via canals for discharge in currently uncontaminated parts of the Everglades. Although this may achieve short term goals of providing more water to pristine areas such as ENP, it would likely lead to extensive contamination of portions of ENP with sulfate, triggering MeHg production and bioaccumulation in fish and other wildlife (Fig. 6). There is already some evidence of canal water containing sulfate entering ENP down the L67 canal. Increases in MeHg levels of fish in ENP have been reported recently (Axelrad et al., 2007).

3.5. Control of dry/rewet cycles – Another water management issue of concern with respect to sulfate sources is control of dry/rewet cycles. The USGS and the Smithsonian Institution have jointly examined the impacts of dry rewet/cycles on the geochemistry of the Everglades, in both field and laboratory studies (Krabbenhoft and Fink, 2001; Gilmour et al., 2004). Results of these studies show that drought (or fire) followed by rewet causes: (1) oxidation of organic soils (peats), transforming reduced S in sediments (organic sulfur and metal sulfides) to sulfate, (2) remobilization of this sulfate into the water column following rewetting, and (3) stimulation of MSR and MeHg production from the remobilized sulfate (Fig. 7). The fire/drought model linking sulfur and MeHg production has important implications for management of the Everglades and STAs, especially STAs that are routinely dried by surface water draw down. Problems with STA 2 producing periodic large plumes of MeHg were shown to be linked to routine dry down and rewet cycles. Limiting dry/rewet cycles in STA2 resulted in much lower levels of
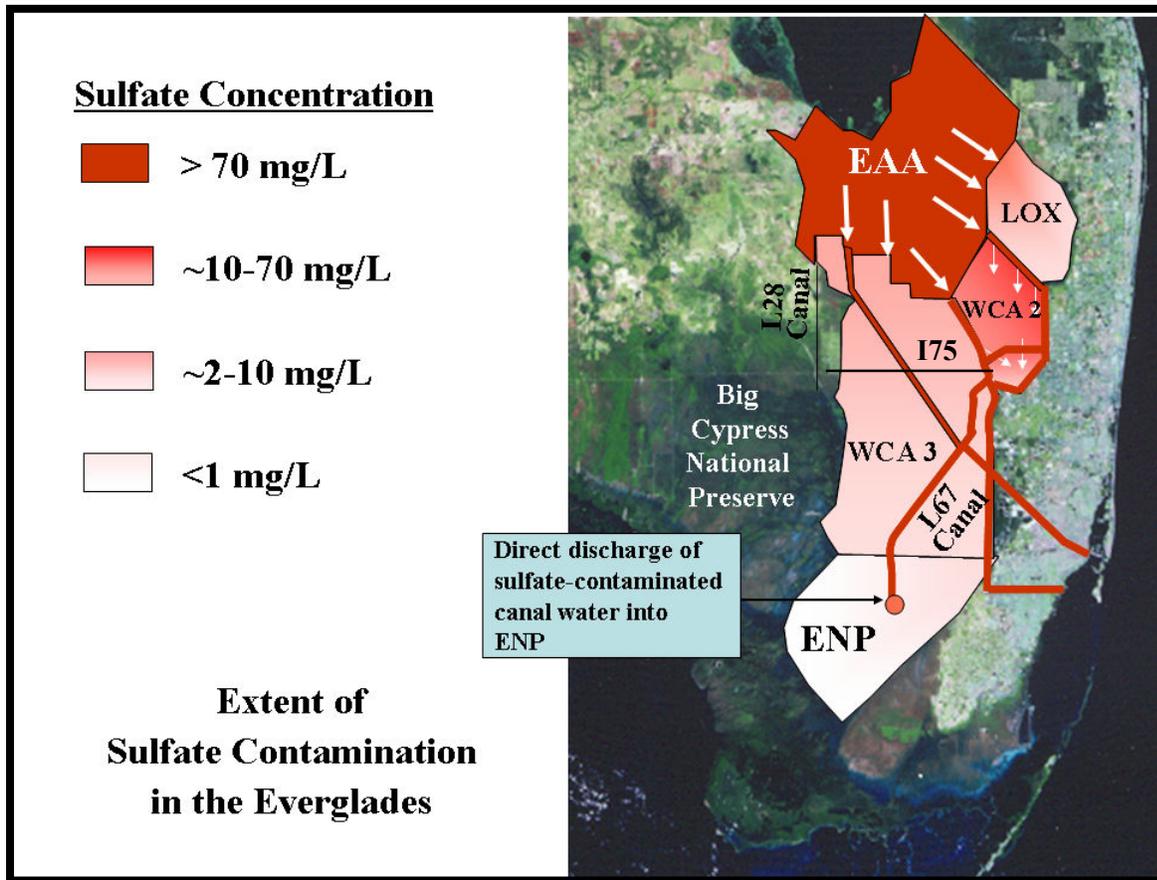
Fig. 6. Extent of sulfate contamination in the Everglades Water Conservation Areas (WCA 1, WCA 2, WCA 3), and in Everglades National Park (ENP). Direct routing of sulfate-contaminated canal water into ENP may lead to unwanted impacts on this pristine part of the Everglades, including enhance production and bioaccumulation of methylmercury.

MeHg production. This also applies to the greater Everglades, especially those areas with elevated sedimentary sulfur resulting from decades of elevated surface water sulfate loading. Although dry/rewet cycles are a natural phenomenon in the Everglades, present conditions of sulfur-contaminated sediments and high atmospheric mercury deposition exacerbate MeHg production and bioaccumulation in these dry/rewet cycles.

4. Biological Mitigation of Sulfate

4.1 Sulfate uptake by plants – Sulfur is an essential nutrient for plant growth, and a major component of amino acids (e.g. cystine, cysteine, and methionine) that are important for protein production and for promoting the activity and development of enzymes and vitamins, as discussed earlier. Sulfate is
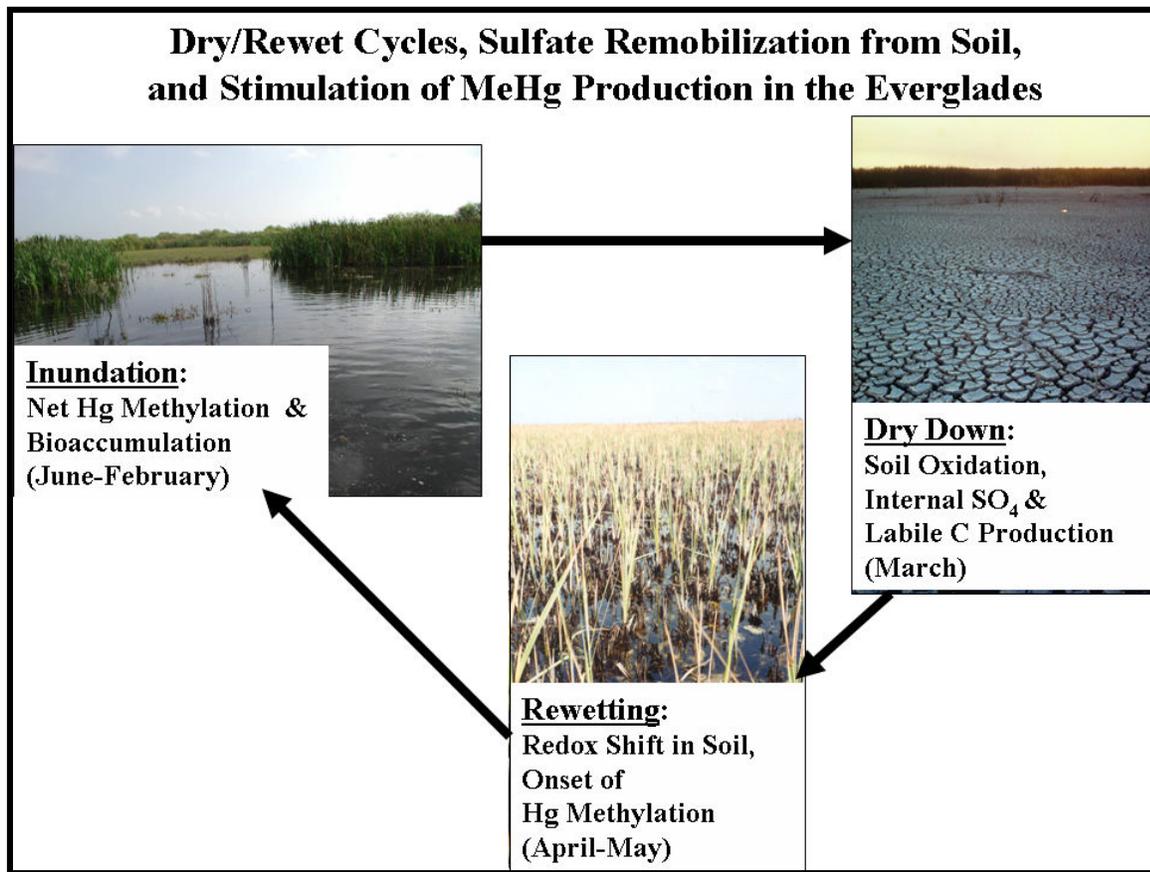
Fig. 7. Dry/rewet cycles as a source of sulfate to the Everglades. Limiting dry/rewet cycles may have benefits for sulfate remobilization from organic soils and for minimizing MeHg production and bioaccumulation in the Everglades (Figure courtesy of D. Krabbenhoft, USGS).

normally taken up by the roots of plants (Cram, 1990; Clarkson et al., 1993), although there is also evidence of direct uptake of atmospheric sulfur (hydrogen sulfide and sulfate) by leaves (De Kok, 1990; De Kok et al., 1997, 1998, 2000, 2002; De Kok and Tausz, 2001; Stuiver and De Kok, 2001). Uptake of sulfate in roots occurs across the plasma membrane of root cells. After uptake, sulfate is (1) transferred to the xylem tissue, (2) transported to the shoot by transpiration, and (3) transported to chloroplasts where it can be used in amino acid synthesis. Uptake of sulfate by plants and its transport to chloroplasts depends on a gradient in protons (co-transport of protons and sulfate) generated by energy-producing ATP degrading enzymes. In chloroplasts, sulfate is reduced to sulfide which is then used to form cysteine, the building block for all other sulfur-containing organic molecules in plants. Sulfate levels in the cytoplasm are kept relatively constant, and excess sulfate is shunted to vacuoles for storage. In short, sulfate assimilation involves uptake by roots, reduction to sulfide in the plant chloroplasts, and conversion to organic sulfur compounds.

The rate of uptake and assimilation of sulfur depends on a number of factors, including the stage of development, plant species, and environmental conditions, especially sulfate concentrations (De Kok et al., 2002). Sulfate concentrations may impact uptake rates via activation and deactivation of enzymes involved in sulfate uptake, through transport by metabolites (Hell et al., 2002) and by metabolite-induced expression or derepression (activation of a gene previously switched off) of genes that encode for sulfate transport enzymes (Hawkesford and Wray, 2000). At least five gene groups have been identified that are involved in sulfate transport in plants. Environmental conditions may also alter sulfate uptake by changing plant growth patterns such as root development and shoot/root ratios.

The maximal sulfate uptake rate by plants is generally reached at sulfate levels of 0.1 mM (9.6 mg/L) or lower. Wetland plants in the Everglades currently take up too little sulfate to significantly impact sulfate levels in the ecosystem. Sulfate requirements of these plants are in the 100s of µg/L range, whereas sulfate levels in much of the ecosystem are in 10s of mg/L. By comparison, phosphate enters the ecosystem in canal discharge at levels of 10s of µg/L (ppb) and is efficiently stripped from the water by wetland plants. The high levels of sulfate also repress uptake of sulfate by wetland plants (De Kok et al., 2002).

Genetic engineering provides a potentially powerful new tool for increasing the capacity of plants to take up pollutants such as sulfate (Kredich, 1993; Stulen and De Kok, 1993). Engineering plants for overexpression of rate-limiting enzymes may accelerate the flux through the entire pathway of sulfate assimilation. A recent study has shown that plants may be engineered to increase uptake of Se (Krämer and Chardonnens, 2001). Uptake of Se proceeds via the same pathway as sulfate uptake (plants mistakenly taking up SeO_4^{2-} instead of SO_4^{2-}): (1) active transport into plant cells by sulfate permease, (2) activation to form adenosine-5'-phosphosulfate by ATP sulfurylase, and (3) reduction to sulfite by APS reductase. The uptake and assimilation of selenate and sulfate are generally assumed to follow the same pathway. Transgenic plants were engineered for overexpression of ATP sulfurylase and accumulated 2-3 times more Se than controls. It may be possible to engineer transgenic plants for increased assimilation of sulfate using this bioengineering approach. Enhancement of phosphorus removal using specific genotypes of sugarcane in the EAA is currently in development (Glaz et al., 2000).

4.2 Microbial removal of sulfate – Microbial removal of sulfate primarily involves reduction of sulfate to sulfide via MSR, and reaction of sulfide with metals to form metal sulfides (e.g. reaction with iron to form iron monosulfides such as Mackiniwite and iron disulfides such as pyrite) or with organic matter to form organic sulfides. This process requires anoxic conditions, which are often encountered in wetland soils, both for MSR (all SRB are obligate anaerobes) and for sequestration and stable storage of the metal sulfides and organic sulfur compounds. In low iron, but high organic matter (peat) systems such as the

Everglades, the dominant form of sulfide sequestration in soils is the formation of organic sulfur species (Altschuler et al., 1983; Bates et al., 1998). Sulfide may react with the solid phase peat (Casagrande et al., 1976 and 1979; Casagrande and Ng, 1979; Brown, 1985 a, b; Brown and Macqueen, 1985; Wieder and Lang, 1988; Novak and Wieder, 1992) or with pore water dissolved organic matter (Heitmann, 2005) to form aryl sulfides, disulfides, thiols, and possibly thiophenes. In this manner, substantial portions of sulfate entering a wetland soil may be sequestered in the soil (Morgan, 1990, 1995; Morgan and Good, 1988).

A number of factors limit MSR and sequestration of sulfur in soil. Sulfate is almost always more limiting than organic matter to MSR (Smith and Klug 1981; Kuivila and Murray, 1984; Carignan, 1985). Since the sulfate source in the Everglades is surface water and MSR occurs in the anoxic soil, a major rate limiting factor is diffusion of sulfate into the soil. Diffusion of sulfate into soils or sediments is typically a very slow process, with diffusion coefficients in marine sediments in the range of 4 to 5 x10^{-6} cm^2 s^{-1} (Li and Gregory, 1974; Krom and Berner, 1980; Ullman and Aller, 1982). The slow diffusion of sulfate into wetland soils is a major reason that sulfate contamination extends over 60% of the Everglades. In contrast, excess phosphorus, which is actively removed by aquatic macrophytes, contaminates <10% of the Everglades. The availability of metals for reaction with sulfide to form insoluble metals sulfides is another factor that limits sequestration of sulfur in wetland soils, especially in iron-poor carbonate ecosystems such as the Everglades. The availability of iron likely increases sequestration of sulfur in wetland soils as metal sulfides (mono- and disulfides) and may also reduce the effects of increased phosphorus remobilization from soils by internal eutrophication (Lamers et al., 2002). In the Everglades most sulfur appears to be sequestered in the soil by reaction with the organic peat to form organic sulfur species (Bates et al., 1998). The short residence time of water (allowing for sulfate diffusion into soil) in STAs and iron limitations are likely reasons for the limited effectiveness of these structures for removing sulfate from inflowing water. Periphyton-based STAs (PASTAs) are STAs dominated by periphyton (algal) growth rather than macrophytes (Bays et al, 2001). These systems may be more effective at generating anoxic conditions near the sediment/water interface (Dodds, 2003), possibly facilitating more efficient sequestration of sulfur via MSR. Further testing of this hypothesis is needed.

Many wetlands are able to sequester significant amounts of incoming sulfur. Volk and others (2003) observed that wetlands were able to reduce sulfate levels by about 50% (1.4 mg/L to 0.65 mg/L for one source, and 2.6 to 1.25 mg/L for a second source). A number of studies have documented from 8 to 80% retention of inflowing sulfate in wetland soils (Hemond, 1980; Braekke, 1981; Calles, 1983; Urban et al., 1986; Bayley et al., 1986). Sulfate retention in wetlands is typically lower in systems with faster flow rates (low retention time) that limit the time for sulfate to diffuse into underlying soils where reduction to

sulfide and sequestration can occur (Bayley et al., 1986). Reducing flow (increasing residence time) and possibly adding an iron source could be ways of improving STAs capacity for retention of inflowing sulfate. Using a push/pull approach involving direct injection of surface or groundwater into wetland soils, Whitmire and Hamilton (2005) achieved a removal rate of 0.7 to 2.4 mg $(SO_4)^{2-}$-S/L-day . At sites in Water Conservation 2A, Fisher and Reddy (2001) observed a relatively rapid sulfate consumption rate via MSR of 130 mg/m^2-day.

Bioreactors have also been used to reduce sulfate in natural waters. Dries and others (2004) used a granular bed reactor, inoculated with acclimated sulfidogenic granular sludge and fed with acetic acid in order to remove sulfate from feed water via MSR. This approach was 80-90% effective (after 60 days operation) in removing sulfate from feed water with a loading rate of 10.4 g $(SO_4)^{2-}$-S/L-day. Levels of acetic acid and pH (slightly basic) were important factors in keeping sulfate removal efficiency high in this approach. Under these conditions, sulfate reduction was carried out primarily by acetotrophic sulfate reducing bacteria. Long-term declines in sulfate removal efficiency in this approach appear to be due to biomass washout and deterioration of the granule supports at high flow velocities. Most bioreactors use a packed-bed reactor with the addition of an external carbon source, such as methanol or acetic acid. Natural reactor media (e.g. crushed limestone and peat) can be used, which is frequently available on-site.

4.3 Permeable Reactive Barriers – One of the newer approaches for passive treatment of contaminated water supplies is the use of permeable reactive barriers (PRBs). This is an in situ process that uses a barrier or treatment zone that is reactive with the contaminant of concern, but permeable to allow the passage of water through the zone. Most PRBs have been applied to remove contaminants from groundwater, but redesign for treatment of surface water is certainly possible. The reactive barrier may be made of materials for the chemical sequestration, chemical breakdown, or microbial breakdown of the contaminant (Scherer et al., 2000). PRBs that have been used successfully include treatment zones or barriers containing zero-valent iron, metal chelators, sorbent materials, and microbial consortia for decomposition of contaminants. Typical applications have included removal of chlorinated hydrocarbons and other organics, radionuclides, and various metals from groundwater. Fluid flow management is essential for water flow via hydraulic head or gravity through PRBs. PRBs can be permanent or semi-permanent treatment devices, depending on the application. In some cases, PRBs are replaced periodically to maintain their contaminant removal efficiency. For example, PRBs using zero-valent iron for removal of chlorinated hydrocarbons may experience clogging from buildup of mineral phases within the treatment barrier (Gu et al., 1999).

Several PRB designs are currently in use. The most common type is a continuous ditch backfilled with the treatment barrier and oriented perpendicular to the flow of water. The so-called funnel and gate approach uses a non-permeable barrier to funnel the water to a permeable barrier where treatment takes place (Lai et al., 2006). Above ground PRBs have also been used in cases where in situ treatment is impractical. About 100 PRBs are currently operating in the USA, with several dozen additional PRBs operating overseas (primarily in Europe).

Inorganic substances, including sulfate, have been successfully removed from contaminated water using PRBs (Blowes et al., 2000). Lai and others (2006) used a funnel and gate type PRB with a zero-valent iron reactant in the treatment zone to remove chlorinated hydrocarbons (>90% removal efficiency) from a contaminated groundwater site in Denmark. The treated water also showed nearly 70% removal of sulfate from the treatment water exiting the PRB. Precipitation of authigenic mineral phases in the PRB caused a decrease in porosity of about 0.9% per year, suggesting that replacement of the PRB will be necessary at some point (probably >20 years) to maintain water flow. Waybrant and others (1998) used mixtures of organic materials in a PRB to promote microbial sulfate reduction. This system had a hydraulic conductivity of 10^{-4} to 10^{-2} cm/sec. Sulfate levels in treatment water in this study were reduced from 4,800 mg/L to <10 mg/L after 65 days of operation. In a similar study, Benner and others (1999) used a wall-type PRB (20 m wide, 3.5 m deep, and 4 m thick in the direction of groundwater flow) filled with organic and inorganic debris (compost, mulch, wood chips, gravel, and limestone) and capped with clay (limits oxygen penetration) to mitigate metals and acid mine drainage in groundwater. Sulfate concentrations decreased from >2,500 mg/L in the treatment water to <500 mg/L downstream of the PRB due to enhanced microbial sulfate reduction and precipitation of iron monosulfides within the PRB. The barrier also removed metals (Fe, Ni) and decreased acidity in the treatment water. Although organic matter-containing PRBs supporting microbial sulfate reduction have the potential for removing sulfate from treatment water, the effect of metal sulfide precipitation on barrier conductivity and long-term hydraulic performance has not yet been determined. These barriers are likely to be viable for at least several decades, however (Benner et al., 1997).

One problem with the organic substrate PRBs for sulfate removal is their tendency for declining performance over time (Cocos et al., 2002; Webb et al., 1998; Blowes et al., 2000). This may be due to limitations in the availability of organic substrate, nutrients (N and P), or an electron acceptor (sulfate). As mentioned earlier, sulfate availability for MSR is usually limited by the slow rate of diffusion or advective flux from the sulfate pool to the anaerobic environment. Substrate and nutrient availability is limited by production from other microorganisms through decomposition of complex organic biopolymers (cellulose, etc.). SRB depend on the production of simple organic molecules (e.g. low molecular weight fatty acids) from biopolymers, usually by fermentation (Widdell, 1988). An

examination of the decline of sulfate reduction in organic substrate PRBs showed that the most important factor was biodegradation of cellulose by the celluolytic microbial community (Logan et al., 2005), which limited the availability of fatty acid substrate (especially lactate) for MSR.

The use of PRBs for mitigation of sulfate contamination in the Everglades would likely require some reengineering, as these devices are usually emplaced within a sediment or soil column to mitigate contaminants in groundwater flow, whereas sulfate contamination of the Everglades is primarily a surface water issue. Possibly a type of PRB (or series of PRBs) could be designed to be emplaced within canals draining the EAA, or emplaced within pumping stations in some manner (Fig. 8). This becomes as much an engineering issue as a biogeochemical one. Both the zero-valent iron and the organic biomass PRBs could be useful approaches for sulfate mitigation and merit further investigation.
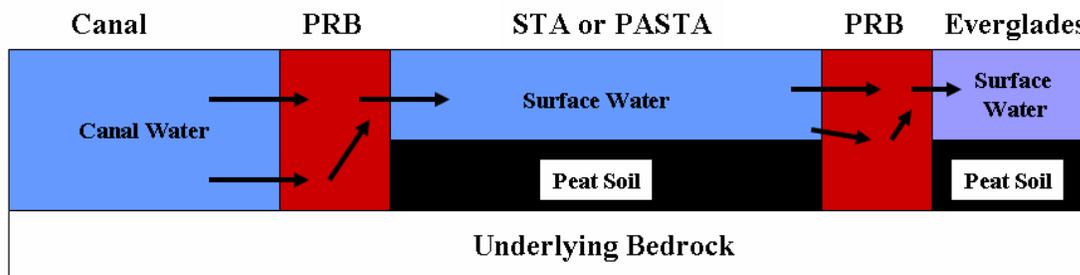
Fig. 8. Possible configuration for use of PRBs in conjunction with STAs or PASTAs for removal of sulfate by reduction to sulfide via MSR, and sequestration through formation of organic sulfur species or metal sulfides. The PRBs could be composed of a mix of crushed limestone, organic muck, and zero-valent iron.

5. Mitigation of Sulfate with Natural Minerals

5.1 Limestone neutralization - Limestone neutralization is a method used to remove acidity from wastewater, such as acid mine drainage (Geldenhuys et al., 2003). Typically, a fluidized bed reactor with limestone particles < 4 mm in diameter is employed. The process has the added advantage of removing some sulfate as gypsum (Maree et al., 2004). This process acts only as a pre-treatment, as it will not reduce sulfate levels appreciably, except for wastewaters with extremely high levels of sulfate (not encountered in the Everglades). It has the benefit of being relatively inexpensive, especially with limestone being readily available in south Florida. Also, pH levels are stabilized by the limestone's natural buffering capacity.

5.2 Feldspar ion exchange – In one study (Priyantha and Perera, 2000), feldspar was shown to effectively remove 34-57% of dissolved sulfate from various industrial wastewater streams over a sulfate concentration range of 1 to 75 mg/L. Feldspar was also shown to remove 38-53% of the phosphate in these effluents. The process employed used feldspar (the most abundant mineral in igneous rock) packed in columns. Effluent was run through the column at different flow rates $(10 – 2 \, cm^3 \, min^{-1})$. The efficiency of sulfate and phosphate removal was greater at lower flow rates. Instrumental analysis revealed that the principal mode of removal of phosphate and sulfate was ion exchange and adsorption. Removal of sulfate and phosphate from the wastewater stream followed first order kinetics. The study provided no information on how long the feldspar will retain sulfate and phosphate removal efficiency before replacement or recharging of the feldspar would be needed. Further study would be needed to determine the replacement time, and cost/benefits of this sulfate removal approach.

5.3 Zeolites – Porous, crystalline hydrated alumino-silicate minerals referred to as zeolites are frequently used in water purification applications (Babel and Kurniawan, 2003). Zeolites can remove ions from water by acting as molecular sieves, sorting ions based on size exclusion. Zeolites have a very regular pore structure at the molecular level, permitting retention of ions that can fit through the molecular pores based on size. Zeolites occur naturally and can be mined, but synthesized zeolites are more often used in water purification due to the presence of unwanted contaminants in some natural zeolites. In addition, manufactured zeolites with properties for specific purification applications have been developed; about 1500 types of manufactured zeolites are available commercially. Clinoptilolite-dominated zeolites modified with the quaternary amine hexadecyltrimethylammonium or HDTMA have been shown to remove sulfate and other oxyanions from water (Haggerty and Bowman, 1994). Removal of the oxyanions from aqueous solution appears to proceed via formation of an anion-HDTMA precipitate on the surface of the zeolite.

6. Mitigation of Sulfate Using Chemical Treatment

6.1 Barium sulfide treatment - This in an interesting approach to sulfate removal from water that relies on the insolubility of barium sulfate in water (Maree, 1991). It can be used in combination with limestone neutralization (see section 5.1). The sulfate-containing water for treatment is dosed with barium sulfide. Carbon dioxide is bubbled through the system to keep the pH acidic (close to pH 5). The barium reacts with the sulfate in the treatment water and barium sulfate is precipitated. The sulfide from the barium sulfide that was added converts to H_2S by reaction with water under the acidic conditions, and is bubbled from the water to the atmosphere with an air stripper. The treatment water is sent to a neutralization tank

or reservoir where lime is added, or run through a limestone neutralization system to adjust pH to near neutral. The treatment water may then be released to the system. The precipitated barium sulfate may be collected and disposed of, or may be regenerated to barium sulfide by heating in a kiln to 1200 °C using natural gas and petroleum coke.

The process may reduce sulfate in treatment water to relatively low levels (e.g. about 5 mg/l). It is also possible to use barium oxide or barium carbonate in this process instead of barium sulfide. Heavy metals are often co-precipitated with the barium sulfate. The formation of insoluble barium sulfate is fairly rapid, and the removal (precipitation) of the barium sulfate from the treatment water can be monitored using a turbidometric approach.

7. Mitigation of Sulfate by Active Removal Processes

7.1 Membrane filtration - Membrane filtration employs semi-permeable membranes that are selectively permeable to water and certain solutes in order to separate various ions or molecules from water (Mulder, 1991). Several different types of membrane separation have been developed, including: ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis. Ultrafiltration is usually used for the separation of large colloidal molecules from aqueous solution (such as organic colloids), and will typically not reject most simple ionic species such as sulfate. Thus, ultrafiltration is not useful for the removal of sulfate from water. Nanofiltration and reverse osmosis are both useful approaches for removal of sulfate from water, with nanofiltration more frequently employed for removal of sulfate. In electrodialysis ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient. The charge on an ion allows it to be driven through the membranes fabricated from ion exchange polymers. Applying a voltage between two end electrodes generates the potential field required for this. Since the membranes used in electrodialysis have the ability to selectively transport ions having positive or negative charge and reject ions of the opposite charge, useful concentration, removal, or separation of electrolytes can be achieved by electrodialysis.

Nanofiltration (Fig. 9) employs membranes having micropores with an average diameter of approximately 10 angstrom or 1 nm between chains in a swollen polymer network. It is a pressure driven process falling between ultrafiltration and reverse osmosis in terms of pressures employed, and membrane pore size. The membranes used for the separation often consist of a thin film polyamide layer bonded to a porous support (Redondo and Lanari, 1997). These membranes exhibit very good separation for selected large ions such as sulfate (Ahu et al., 1999). Nanofiltration is most effective for removal of di- and multi-valent anions, and for dissolved organic matter with a molecular weight >300. FilmTec Corporation (Minneapolis, MN) nanofiltration membranes NF-40 or NF-50 have been found to be particularly
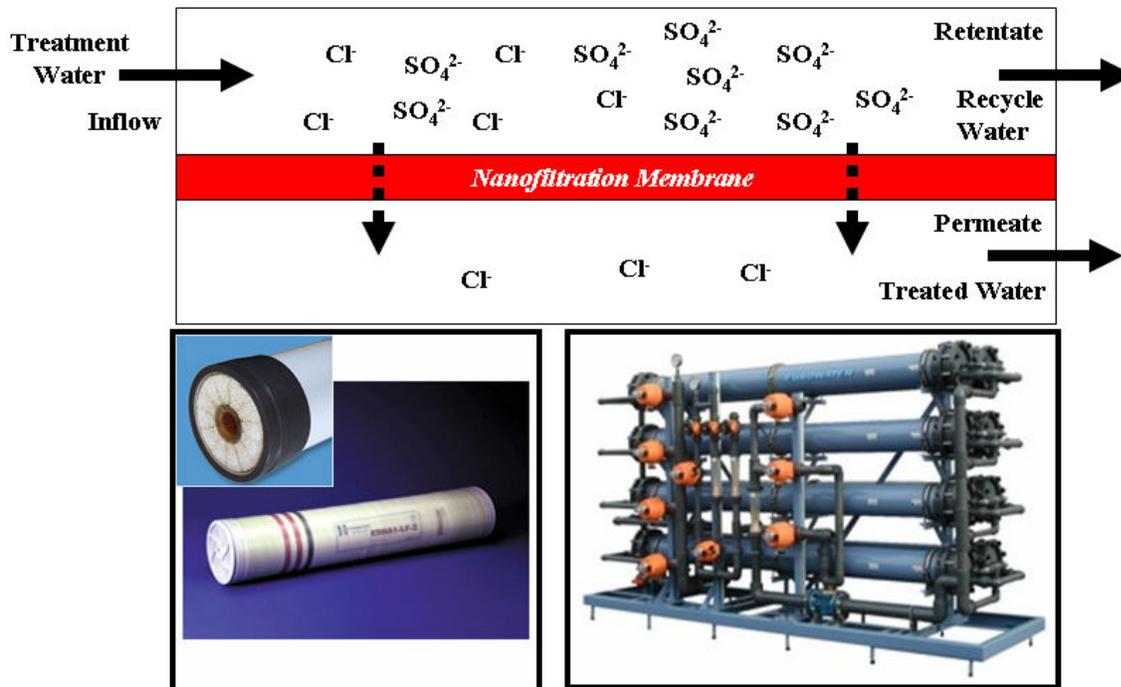
Fig. 9. Principle of nanofiltration (top diagram), and pictures of nanofiltration membranes and a nanofiltration array for treatment of water. Figure adapted from Eurowater (www.eurowater.de).

effective in removing a high proportion of the sulfate ions (and other large, divalent anions and cations) from water. Nanofiltration membranes are available and used in the following modes: (1) a simple plate and frame constructions with the membrane on top of the plate, (2) spiral wound modules, (3) hollow fibers, and (4) arrays of tubular membranes. Spiral wound membrane devices are most often used for removal of sulfate from water (Bertrand et al., 1997). Nanofiltration has been used for the removal of color and total organic carbon from surface water in Florida, removal of sulfate and radium from well water, removal of sulfate from seawater (Eriksson, 1988), and removal of sulfate from oilfield brines (Bakke et al., 1992). A study of drainage from South African gold and coal mines found that nanofiltration reduced sulfate levels in the drainage water by 95-99% (Visser et al., 2001). The cost of a nanofiltration facility is approximately the same as that for a reverse osmosis plant for desalination of brines; however, energy costs for nanofiltration are significantly lower than those for reverse osmosis (Le Gouellec de Schwarz, 1998).

Although membranes are very effective at removing sulfate from water, this approach suffers from a number of disadvantages. The membranes are relatively expensive, and require continuous application of pressure. Pressure is usually applied by some type of electric pump, with additional expense resulting from power consumption. Membrane approaches have been extremely effective at removing ions from seawater in desalination plants and sulfate in agricultural runoff (Le Gouellec and Elimelech, 2002; Le

Gouellec de Schwarz, 1998). Wetland waters have significantly higher levels of particulate and colloidal materials, and dissolved organic substances, leading to problems of clogging of the membrane pores and biofouling (Gilron and Hasson, 1987; Nystrom et al., 1995). Generally, the more contaminated the feed water and the higher the desired water quality, the greater the likelihood of membrane fouling caused by particulate matter, scaling and biofouling. One potential solution to membrane fouling is to use an advanced pretreatment process prior to nanofiltration or reverse osmosis treatment. Pretreatment systems involve a series of membranes of gradually increasing selectivity, and are often referred to as integrated membrane systems (Reiss et al., 1999). Capital costs for nanofiltration is high, but additional modular components can be added to increase treatment capacity at limited additional cost. Operating costs for nanofiltration are relatively high because operation requires some technical skill and routine monitoring of performance.

7.2 Ion exchange - In ion exchange, water containing an ion of interest (e.g. sulfate) is passed through a resin that is specifically designed for the removal of the ion of interest (Wachinski and Etzel, 1997). As water passes through the resin, the ion of interest is exchanged for an ion on the resin, usually chloride in resins for sulfate ion exchange, thus removing sulfate from the water sample. The proper selection of the sulfate removal resin is of primary importance and so-called strong base resins are usually employed, such as Dowex Monosphere 77 and M-31, and Dowex 1 and M-31 (Lee and Bauman, 1983a and b). These resins are designed to tightly bond the ion of interest (sulfate) until regeneration of the resin. Some commercial resins are reported to be effective at removing essentially 100% of the sulfate in a water sample with sulfate concentrations up to 2,500 mg/L. Factors such as high levels of dissolved organic carbon or high particulate load, however, can impact the efficiency of these resins by adsorbing to the resin and preventing exchange of ions. The resins may be regenerated using a brine solution, which displaces the sulfate ions and replaces them with chloride. Both ion exchange and nanofiltration are efficient at removing sulfate from water, but Darbi et al. (2003) suggest that ion exchange may be the preferred approach for natural waters due to problems in nanofiltration associated with high particulate load and biofouling of membranes. Both nanofiltration and ion exchange efficiency are impacted by high dissolved organic matter content in natural waters.

8. Conclusions

Sulfate is entering the freshwater Everglades at unnaturally high levels, as high as 60 to 100x background levels, and impacting an estimated 60% of the area of the ecosystem. Sulfate has a number of serious impacts on the ecosystem, including: (1) stimulating MSR, which controls the methylation and bioaccumulation of neurotoxic MeHg in the Everglades, (2) generating toxic hydrogen sulfide in

Everglades soil, which has dramatically lowered redox conditions and is toxic to some macrophytes (e.g. *Cladium*), and (3) increasing the rate of release of nutrients (phosphorus and nitrogen) from soils in a process termed internal eutrophication. Additional impacts on fauna, flora, microbial assemblages, and trace metal cycling are currently being evaluated. Indeed, the argument can be made that sulfate represents a more serious water quality problem for the Everglades than phosphorus contamination because of the level of contamination, the aereal extent of contamination, and the myriad impacts of sulfur on biota.

Sulfate enters the Everglades almost entirely via discharge of contaminated canal water. The source of the sulfate in the canal water remains somewhat controversial, but currently available data suggest that a significant portion of it originates from recent and historic uses of sulfur in agriculture in the EAA. Strategies for mitigation of sulfate contamination of the Everglades could logically start with minimizing anthropogenic uses of sulfur that could enter the ecosystem. This would likely require the cooperation of the agricultural community in the EAA and north of Lake Okeechobee, agricultural researchers, manufacturers of agricultural fertilizers and soil amendments, water and land managers, wetlands scientists, and government officials. Further research to refine the amounts of sulfate coming from the EAA, groundwater, and elsewhere would certainly be needed. Agricultural research to determine the minimum sulfur requirements of crops grown in the EAA, and of grasslands for cattle north of Lake Okeechobee could be considered (data on this may already exist to a large extent). Anthropogenic use of sulfur-containing chemicals in agriculture needs to be evaluated in order to balance adequate sulfur nutrition for crops (sugarcane and vegetables) and grass with minimizing sulfate runoff and resulting impacts on the Everglades. It may be that sulfur already bioavailable in agricultural soils is sufficient to fulfill the needs of various crops. In some instances, fertilizers are added with sulfur in the mixture as an addition to the main element, or as a counter-ion in the mixture (e.g. ammonium added as ammonium sulfate to grazing fields, or metals added as metal sulfates to EAA crops; see Table 1). If these sulfur additions are determined to be unnecessary for plant nutrition, then substitution of more inert chloride as a counter-ion could be implemented at the manufacturing level. Fungicides are another source of sulfur to the ecosystem, especially the use of elemental sulfur as a broad spectrum fungicide and copper sulfate as a fungicide in citrus production. More environmentally innocuous alternatives could be considered, especially bioengineered fungicides that are specific for a particular fungus type. In the case of copper sulfate, cupric chloride could be considered as an alternative, although Cu itself has unwanted environmental effects (Flemming and Trevors, 1989; Leslie, 1990). As noted earlier, any reductions in anthropogenic sulfur use will benefit the ecosystem.

Currently available data do not support groundwater as a major source of sulfate to the ecosystem. This is excluding possible sulfur sources from aquifer storage and recovery. If groundwater is shown to

be a significant source, then approaches for reducing groundwater fluxes (especially deep groundwater >9 m, which has very high levels of sulfate) could include reducing any unnecessary groundwater usage, and repairing leaky canal bottoms.

There is probably little that can be done to reduce sulfur sources from soil oxidation in the EAA and elsewhere in the Everglades' watershed. This soil sulfur represents sulfur that was applied for agricultural purposes (new and legacy) and natural sulfur in the soil. Agricultural practices in the EAA are dependent on a dry and oxic surface layer of soil. Microbially mediated oxidation transforms most of the sulfur in this layer to sulfate, which is readily washed into canals during rain events. Maintaining reducing conditions in surface soils by waterlogging would prevent oxidation of reduced sulfur species, and effectively sequester sulfur in the soil, but most crops cannot be grown under such conditions. Unless water tolerant sugarcane can be developed, oxidation of EAA soil will likely continue. Rotation of rice with sugarcane, however, does help the situation by reducing oxidation during the period of rice cultivation.

In addition to reducing anthropogenic uses of sulfur, it is likely that active mitigation strategies will be needed to reduce sulfur loads to levels that will significantly benefit the Everglades ecosystem. A number of different mitigation approaches have been briefly outlined in the preceding sections of this report. Strategies range from passive approaches such as the use of minerals that absorb sulfate, or anaerobic microbial processes to sequester sulfur, to more active (and expensive) approaches such as nanofiltration or ion exchange. The relative merits of the various mitigation strategies in terms of effectiveness in removing sulfate and cost (initial and ongoing costs) are summarized in Table 2.

The current configuration of existing macrophyte-dominated STAs appears to have limited capacity to sequester sulfate as reduced sulfur species in soils. This is probably due to three factors: (1) the slow rate of diffusion of sulfate into sediments where MSR and sulfur sequestration occurs, (2) inefficiencies in the microbial consortia that supports MSR , especially in regard to cellulose decomposition, and (3) limitations in the availability of iron for the sequestration of reduced sulfur species as iron mono- and disulfides. Periphyton-dominated STAs (PASTAs) may be more efficient at removing sulfate through formation of extensive anoxic floc layers at the sediment/water interface. These floc layers may enhance sulfate diffusion to sites of MSR. Also, the algal material is more biodegradable than vascular plant-derived organic matter from macrophytes and may stimulate production of organic substrate supporting MSR. The efficiency of PASTAs in removing sulfate, however, is unclear at this time. Studies of sulfate removal efficiencies in macrophyte-dominated STAs versus PASTAs would provide useful information.

The creation of zones in the STAs or PASTAs that resemble PRBs might also be effective in sulfate removal. Trenches at the ends of STAs and PASTAs composed of organic-rich material and zero-valent iron may increase MSR and sulfur sequestration. One approach for evaluating this could involve initial

Table 2. Relative effectiveness and costs among different active and passive sulfate mitigation strategies for the Everglades (L = Low, M = Moderate, H = High).

Sulfur Mitigation Method	Effectiveness of Sulfate Removal	Initial Costs	Maintenance Costs	Notes
Biological Removal (STAs, PASTAs)	L-H[a]	L-M[b]	L[c]	(a) effectiveness depends on type of STA used, residence time of water, etc. (b) STAs already exist, may require some modification (c) little maintenance cost once operating
Permeable Reactive Barriers (PRBs)	M-H	M[d]	L[e]	(d) construction of barriers from bio-waste, zero-valent iron, and crushed limestone (e) essentially none until replacement is needed
Mineral Removal (limestone, feldspar zeolites)	L-M	M[f]	L[g]	(f) construction of trenches for mineral emplacement (g) essentially none until replacement is needed
Chemical Treatment (Barium Sulfide)	M-H	M-H[h]	M-H[i]	(h) construction of reaction ponds or chambers (i) collection and disposal of precipitated $BaSO_4$
Membrane Filtration (nanofiltration)	H[j]	M-H[k]	H[l]	(j) also removes other ions of concern, e.g. PO_4^{3-} (k) costs include pre-filters, nanofiltration filter setup, pumps, and operator training (l) frequent replacement of nanofilters may be necessary due to biofouling
Ion Exchange	M-H	M-H[m]	M-H[n]	(m) costs include pre-filters, ion exchange cartridges and setups, operator training (n) frequent replacement of pre-filters and ion exchange resins may be needed due to high particulate and dissolved load

laboratory testing with Everglades' canal water, and follow-up field tests in an up scaled PRB. Sequestration of sulfate from canal water could also be achieved using a bioreactor approach, using either addition of barium to precipitate sulfate as $BaSO_4$ under oxidizing conditions, or using a reducing bioreactor to facilitate MSR and sequestration of sulfide. Bioreactor approaches, while effective, would likely be extremely costly to construct, operate, and maintain. They also present the problem of disposal of the precipitated $BaSO_4$ or metal sulfides.

Active mitigation using nanofiltration or ion exchange are extremely effective at removing sulfate from water both at the laboratory scale, and in desalination plants for production of drinking water. Up scaling to the volumes involved in treatment of water from Everglades' canals, however, may be problematic. In addition, issues of biofouling of membranes in nanofiltration or clogging of ion exchange resins would have to be overcome. These approaches may be most effective in controlling sulfate outputs from feeder canals coming from individual farms. Individual farms are locations where sulfate loads may be highest, and water volumes lowest, allowing the most efficient application of the nanofiltration or ion exchange approaches.

The problem of sulfate contamination of the Everglades ecosystem is many decades old, and it will likely take some time to fully address this issue. Observations from this report suggest some possible initial sulfur mitigation strategies: (1) further studies to determine the sources of sulfate would constrain which approaches to reduce these sources would be most effective, (2) explore ways to eliminate or reduce these sources of sulfur, especially through reductions in anthropogenic uses of sulfur, (3) examine biological removal processes, improvements to existing STAs, and PASTAs as sulfate-removal wetlands, (4) examine possible use of PRBs (possibly in combination with STAs or PASTAs) to reduce sulfate loads, and (5) examine the economics and practicality of nanofiltration and ion exchange at the individual farm level for active mitigation. The first three strategies involve the use of existing scientific expertise and infrastructure. If the economics of active mitigation using nanofiltration or ion exchange look reasonable, initial pilot studies could be undertaken.

The success of sulfur mitigation strategies do not depend on attaining pre-development levels of sulfate in the ecosystem. Although this would be desirable, current conditions in the sulfur source areas likely preclude attaining levels of ≤ 1 mg/L sulfate in large areas of the Everglades. Nevertheless, studies in the Everglades have demonstrated that any significant reduction in current sulfate loads to the ecosystem will have beneficial results, especially with regard to levels of MeHg, and that the response of the ecosystem to reduced sulfur loads is likely to be rapid.

9. Acknowledgments

10. References

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